# REACTOR MATERIALS

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by BATTELLE MEMORIAL INSTITUTE

*Spring 1969*

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# TECHNICAL PROGRESS REVIEWS

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# Reactor Materials

is one of a series of quarterly technical progress reviews broadly covering the field of nuclear science and technology. Under the auspices of the USAEC Division of Technical Information, *Reactor Materials* is prepared by Battelle personnel from worldwide literature. It covers properties, behavior, and fabrication processes of materials applicable to nuclear reactor components and associated equipment.

The reader will recognize that the scope of this Review is too broad to permit detailed coverage of every topic. Rather, the authors and editors attempt to combine the highlights of significant new developments into an information summary of current research for both management and the technical specialist. As a rule, enough of the results are presented to define the research and summarize the findings. For readers desiring more information on any particular topic, a complete set of references is provided at the end of each section.

Each quarter a number of bibliographies, monographs, and books appear on subjects within the scope of *Reactor Materials.* Although the main purpose of this Review is to call attention to findings that are new and significant, such publications are noted in the text because they often represent excellent compilations of available information on important materials topics.

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**BATTELLE MEMORIAL INSTITUTE**
**COLUMBUS LABORATORIES**

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Section

I

Reactor Materials

# Fuel and Fertile Materials

## Uranium and Uranium Alloys

### Unalloyed Uranium

The Yugoslavians[1a] studied the thermodynamics of uranium grain growth. The free energy of activation was found to increase linearly with temperature in the interval 450 to 600°C, with the temperature coefficient being 17.3 cal/(mole)(°K) and a mean value for the given interval of 107,750 cal/mole. The free energy of grain growth, the entropy of the system, and the enthalpy of the system were $+3.5 \times 10^{-1}$ cal/mole, $-3.2 \times 10^{-4}$ cal/(mole)(°K), and $+9.3 \times 10^{-2}$ cal/mole, respectively.

Basic information on the deformation mechanisms in alpha-phase uranium is provided by a series of articles in the *Journal of Nuclear Materials*.[2-5] Yoo[2] calculated the effective shear-moduli dislocation-line energies, dislocation widths, and Peierls–Nabarro stresses and substantiated that (0 1 0)[1 0 0] is the primary slip system at room temperature and (0 0 1)[1 0 0] is the secondary slip mode. These calculations also correctly predict the prevalence of (0 0 1)[1 0 0] slip over (0 1 0)[1 0 0] slip above the range 325 to 350°C. The easy-glide parameter for dislocation mobility of various slip systems calculated by the Czechoslovakians[3] from anisotropic elasticity data agrees with Yoo's results. This parameter was used as the criterion for the principal slip system. Figure I-1 shows this parameter for edge dislocation in alpha uranium where the upper curve denotes the operative system. The French[4] also found the same slip systems to be operative by tension testing of single crystals of alpha uranium. The Czechoslovakians[5] also examined the possible dissociation of dislocations on the primary slip systems.

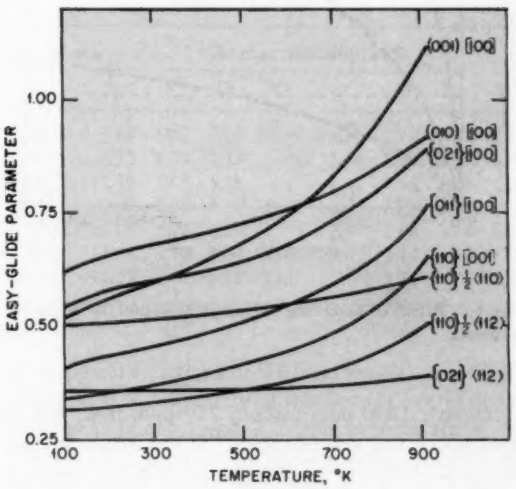


**Fig. I-1 Temperature dependences of the easy-glide parameter for edge dislocations.[3]**

### Alpha-Phase Uranium Alloys

In a study at the University of Florida,[6] alloys with additions of aluminum (203 to 750 ppm), carbon (795 ppm), iron (135 to 287 ppm), and silicon (122 to 399 ppm) resulted in the following conclusions on structural changes associated with deformation at high temperatures.

1. Uranium resembles other metals in most of its high-temperature deformation characteristics.
2. Grain growth accompanies deformation.
3. New grains maintain a size which is larger at higher temperatures and which has slower deformation rates.
4. New grain formation is promoted by alloying that lowers the recovery temperature of alpha uranium.
5. Silicon additions maintain a fine grain size in the alpha uranium during tensile straining and thermal cycling.

The recrystallization kinetics of "adjusted" uranium (700 ppm aluminum and 250 ppm iron) were studied by the British.[7] Figure I-2 shows the recrystallization time at 600, 625, and 650°C. Precipitation of new phases in an adjusted alloy with 710 ppm

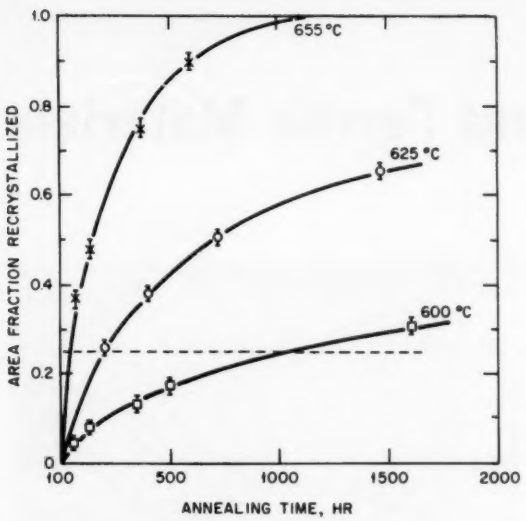


**Fig. I-2 Effect of annealing on recrystallization of "adjusted" uranium.[7]**

aluminum, 1000 ppm carbon, 250 ppm iron, and 50 ppm silicon was also examined.[8] It was concluded that iron and aluminum in adjusted uranium is retained in solution on quenching from the alpha phase and on heating in the alpha region, and only the phase $UAl_2$ precipitates. The time dependence of the precipitation process is consistent with precipitation occurring at subgrain boundaries and on individual dislocations within subgrains. A change in the precipitation rate occurs below about 500°C.

The French[9] investigated the effect of boron on the recrystallization of alpha-phase uranium with 0.2 to 0.4 at.% molybdenum. Small additions (100 ppm) of boron led to pronounced refinement of the alpha grain size even for slow cooling rates. The $UB_2$ precipitates acting as heterogeneous nuclei caused this refinement. The boron also refined the grain structure of dilute U–Si, U–Cr, U–Mo–Al, U–Mo–Si, and U–Mo–Sn alloys as long as the boride particles were finely dispersed.

The Polish[10] determined the effect of 0.5 to 3 wt.% molybdenum on the tensile properties of uranium. It was found that alloying with 1.1 wt.% molybdenum increased the tensile strength of uranium from 36.1 to 94 kg/mm² (51,000 to 133,000 psi) at 20°C and from 5.1 to 20.5 kg/mm² (7200 to 29,000 psi) at 600°C. Further increases in molybdenum content did not have any significant effect on the strength of uranium.

Petzow, Sampaio, and Pinto[11] have presented phase-equilibria data in the U–$UMn_2$–$UFe_2$ and $UAl_2$–$UMn_2$–$UFe_2$ systems. Complete solubility exists between the intermetallic phase $U_6Fe$ and $U_6Mn$, as well as between $UFe_2$ and $UMn_2$. Therefore the two-phase zones alpha uranium + $U_6(Mn,Fe)$ and $U_6(Mn,Fe)$ + $U(Mn,Fe)_2$ dominate almost the entire system at room temperature.

### Delta-Phase Alloys

The Canadians[12] studied the delta peritectoidal reaction in U–Si alloys and concluded that:

1. Carbon concentrations of up to 2000 ppm lower the peritectoid temperature and form a region of three-phase equilibrium between uranium, $U_3Si_2$, and $U_3Si$.
2. The three-phase region has an upper limit of 860°C and a lower limit of 790°C in an alloy containing 2000 ppm carbon.
3. The higher the carbon, up to 2000 ppm, the lower the optimum temperature for transformation to $U_3Si$.
4. Increasing the carbon concentration and thus lowering the optimum transformation temperature do not significantly affect the rate of transformation.

(R. D. Koester and M. S. Farkas)

# Plutonium

### Plutonium Metal and Alloys

Experiments at Rocky Flats have resulted in the successful growth of large crystals of a Pu–3.3 at.% Ga alloy using a modified Bridgman technique.[13] Large polygonized grains (to 6 mm) were grown by slowly transforming an epsilon phase that was created by slow freezing of the melt. Long anneals of over 200 hr resulted in some highly perfect grains.

Ternary U–15 Pu–10 Zr and U–15 Pu–15 Zr alloys* are being prepared at Los Alamos[14] by induction melting both in conventional crucibles and in "cold" crucibles. Homogeneous alloys have been prepared at 1400°C in less than 10 min by mechanical stirring of a melt consisting of plutonium and a prealloyed U–Zr binary. The reaction of crucible materials and coatings with the ternary U–15 Pu–12.7 Zr alloy at 1400°C for short times is being

*Unless otherwise designated, all compositions are understood to be in weight percent.

studied. The most promising crucible coating appears to be a colloidal suspension of $Y_2O_3$ sprayed onto the crucible surfaces. In the cold crucible method, the ternary alloy is prepared by melting and stirring inside a water-cooled metallic crucible. A frozen alloy skin next to the crucible prevents impurity pickup from the crucible.

The Pu–Zr equilibrium diagram up to 10 at.% zirconium developed by Battelle–Northwest (Fig. I-3) differs from previously published diagrams.[15] The existence of a zeta intermediate solid-solution phase (2.5 to 2.7 at.% zirconium) was confirmed. Phase-stability studies indicate that the retained delta phase transforms to beta phase, the rate of transformation decreasing with increasing zirconium content. The retained beta phase is unstable and gradually transforms to alpha phase. The data indicate that the beta-retained Pu–Zr alloy would have limited use as an engineering material due to its instability.

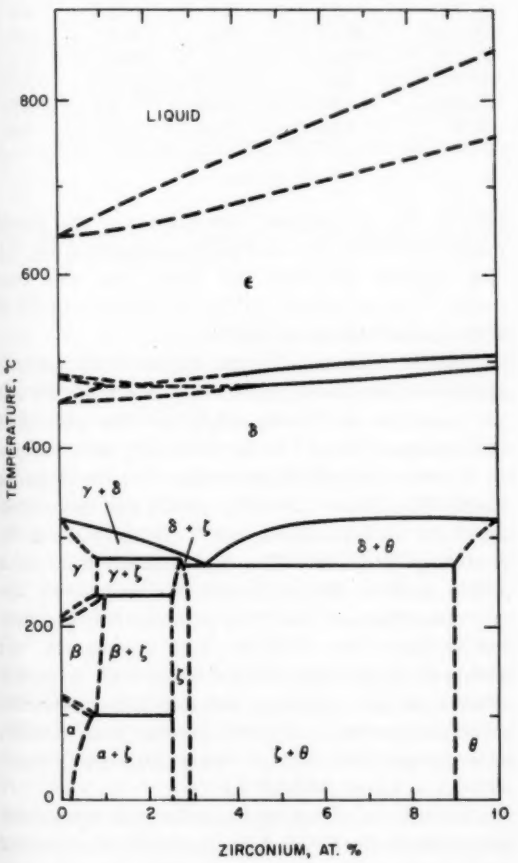


Fig. I-3 Plutonium-rich end of the Pu–Zr equilibrium diagram.[15]

Measurement of the solubilities of various metallic elements in liquid plutonium over the temperature range 700 to 1000°C is continuing at Los Alamos.[16] The data, some of which are summarized in Table I-1,

**Table I-1 Average Solubilities of Selected Elements in Liquid Plutonium[16]**

| Temp., °C | Average solubility, at.% | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| | Ti | V | Cr | Mn | Zr | Nb | Mo | Tm |
| 700 | 5.44 | 1.02 | 1.62 | | 2.10 | 1.10 | 1.57 | 2.35 |
| 750 | 9.72 | 1.34 | 2.23 | | 3.44 | 1.44 | 2.11 | 3.08 |
| 800 | 22.50 | 1.67 | 3.26 | | 5.42 | 1.69 | 2.65 | 4.09 |
| 850 | 26.07 | 2.29 | 4.35 | 30.8 | 8.03 | 2.05 | 3.08 | 5.04 |
| 900 | 28.81 | 2.96 | 5.59 | | 12.4 | 2.68 | 3.64 | 6.79 |
| 950 | 33.31 | 3.78 | 6.94 | 45.7 | 18.0 | 3.14 | 4.58 | 7.25 |
| 1000 | 37.17 | 4.46 | 8.58 | 53.6 | | 3.71 | | 8.48 |

fit empirical equations of the form $\log N_i = A - (B/T)$, where $N_i$ is the solubility of the element $i$ expressed as an atomic fraction and $T$ is the temperature in °K. From these and previously reported solubility data, the relative partial molar enthalpies shown in Table I-2 have been calculated for the simple eutectic-type binary systems indicated.[17]

**Table I-2 Relative Partial Molar Enthalpies of Selected Elements in Liquid Plutonium[17]**

| Element | $\Delta H_i$, kcal/mole |
|---|---|
| Tungsten | 22.0 ± 0.1 |
| Tantalum | 16.6 ± 0.1 |
| Niobium | 11.1 ± 0.1 |
| Vanadium | 11.0 ± 0.1 |
| Molybdenum | 10.3 ± 0.1 |
| Chromium | 9.5 ± 0.1 |
| Thulium | 9.2 ± 0.2 |

Eleven liquid Pu–Co–Ce alloy fuels in tantalum capsules have been irradiated to 2.6 at.% burnup under conditions similar to those expected in the Fast Reactor Core Test Facility.[18] The fuel–container interface temperature was maintained below 725°C but above the fuel freezing point of approximately 440°C. The capsules operated at an average specific power of 150 watts/g of plutonium. Presumably, postirradiation observations will be described in a future report.

Argonne and Battelle–Northwest are initiating a program to determine the mechanism that controls swelling in U–Pu-base fuels and to establish the effects of temperature, pressure, burnup, and fuel composition on the swelling rate.[19a] Injection-cast and heat-treated specimens will be irradiated isothermally and at constant pressure within a range of temperatures from 400 to 800°C and a range of pressures from 50 to 5000 psi. Specimens of uranium, U–5 Pu, U–14 Pu, and U–14 Pu–12 Zr have been prepared and are being encapsulated. Irradiation is expected to begin shortly as reactor space becomes available.

A single unit process for the rapid production of plutonium metal from the oxides has been reported by Lawrence Radiation Laboratory.[20] The process consists in (1) the reduction of the plutonium oxides by calcium metal, (2) the extraction of the CaO reaction product with molten calcium chloride, and (3) the quantitative separation of the two immiscible molten-metal phases by the immiscible salt solution. Yield efficiencies of 99.96% are reported, with a batch cycle time of 15 min independent of batch scale.

(D. F. Askey)

## Plutonium Compounds

### Oxides

Oak Ridge[21] has established the feasibility of producing $PuO_2$ from $PuF_6$. The product from these experimental runs was confirmed by X-ray diffraction examination. A limitation of the vapor fabrication of $PuO_2$ was recognized as the conversion of $PuF_4$ to $PuF_6$, although this aspect of the process was not a part of the experimental process studied.

Spherical particles of $PuO_2$ have been prepared in two laboratories[22,23] by the sol-gel technique. Mound Laboratory[22] has evaluated $^{238}PuO_2$ particles and determined a crush strength of 1260 g and a density of 10.8 g/cm$^3$ for 250- to 400-$\mu$ spheroids that had been calcined at 1200°C. At Karlsruhe,[23] $PuO_2$ microspheres were prepared and reduced in hydrogen at 1750°C to obtain particles with a final O/Pu ratio of 1.67 to 1.73. These particles were subsequently coated with carbon and silicon carbide. Mound Laboratory[24] has also established the impact characteristics of plasma-formed $^{238}PuO_2$ microspheres under simulated reentry conditions. The particle-size distribution before and after impact at 105 ft/sec is shown in Table I-3.

Argonne[25] has measured the high-temperature properties of $PuO_2$. The heat capacity of $PuO_2$ was given as:

$$C_p = 22.18 \times 2.080 \times 10^{-4}\, T - 4.935 \times 10^{5}\, T^{-2}$$

An extrapolation of this relation to higher temperatures resulted in a value of 23 ± 1 cal/(mole)(°K) at the melting point, 2663 ± 20°K. Mass-spectrometric studies performed in iridium effusion cells yielded partial heats of sublimation in kcal/mole for the vapor species: 138.8 ± 1.1 for $PuO_2(g)$, 127.2 ± 2.7 for PuO(g). The temperature dependences of the partial pressures of $PuO_2(g)$ and PuO(g) are shown in Fig. I-4. The thermal diffusivity for $PuO_2$ has also been found[19b] to be 0.0148 cm$^2$/sec at 400°C, 0.00503 at 1500°C, and 0.00400 at 2000°C.

**Table I-3 Effect of Impact on Particle-Size Distribution[24] of $PuO_2$**

| Diameter, $\mu$ | Distribution before impact, wt.% | Distribution after impact, wt.% | | |
|---|---|---|---|---|
| | | Capsule 18 | Capsule 20 | Capsule 24 |
| 177–210 | 8.16 | 9.4 | 7.7 | 5.7 |
| 149–177 | 21.22 | 25.2 | 18.3 | 14.8 |
| 125–149 | 16.53 | 18.1 | 15.9 | 12.1 |
| 105–125 | 18.98 | 12.6 | 14.1 | 14.2 |
| 77–105 | 21.63 | 19.8 | 24.3 | 24.6 |
| 44–77 | 13.47 | 10.4 | 16.9 | 23.1 |
| 20–44 | 0.00 | 3.02 | 0.73 | 3.8 |
| 10–20 | 0.00 | 0.26 | 0.08 | 0.19 |
| >10 | 0.00 | 0.03 | 0.06 | 0.08 |

Mound Laboratory[26] has reviewed the methods applied for the dissolution of $PuO_2$. The solubility rate was found to be directly related to the method of oxide preparation and to the processing temperatures.

A mechanical blending-powder route for preparing mixed $UO_2$–20 to 25 $PuO_2$ pellets has been established by Battelle–Northwest[27] as the process for producing FFTF fuel. The specified limits for these pellets are 93 to 95% of theoretical density and a 50-$\mu$ maximum diameter for $PuO_2$ particles. Nuclear Materials & Equipment Corp.[28] has investigated the incorporation of burnable additions, such as methyl cellulose, sucrose, dextrose, and carbowax, into mixed oxides for porosity and density control. Final densities in the range 85 to 92% of theoretical were obtained with 1.5 to 3.0 wt.% additions.

The effects of selected metallic and nonmetallic impurities on the sintered density of mixed oxides and the retentive ability of the oxides during sintering were studied at Nuclear Materials & Equipment Corp.[29] The chemical analysis before and after sintering showed

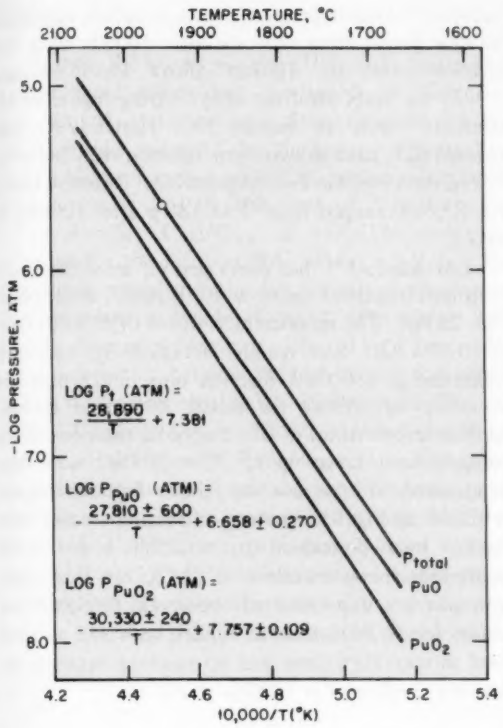


**Fig. I-4 Temperature dependence of the partial pressures of $PuO_2$(g) and PuO(g) (Ref. 25).**

that only two impurities, silicon and chromium in concentrations of 5000 ppm, decreased the sintered density. Losses of 2 to 7% in density were observed, depending upon the particle size of the impurity.

The Babcock & Wilcox Co.[30] has evaluated both gel additions and mixed-sol blending as techniques for producing $UO_2$–$PuO_2$ particles. Gel-addition chemistry studies have involved techniques for improving the pickup of trivalent or quadrivalent plutonium by in situ changes of *p*H and plutonium valence. Adjustments of this type increased the pickup from the range 4 to 5% to between 7 and 10%, which is about half that required for fast reactor fuel. Mixed sols usually undergo segregation unless strongly agitated. $UO_2$–20 $PuO_2$ particles with 95% of theoretical density and 44- to 500-$\mu$ particle size were obtained after sintering at 1250°C in $N_2$–6 vol.% $H_2$. Oak Ridge[21] has also investigated mixed-sol techniques for mixed-oxide preparation. The product is further jet milled, cold pressed, and sintered into cylindrical pellets. Final densities in the range 85 to 90% of theoretical have been achieved.

The diffusion of uranium in $PuO_2$ and plutonium in $UO_2$ has been determined at Karlsruhe[31] by electron-microprobe analysis. The diffusion of these species has been given as: $D_U = 9.25 \times 10^{-5}$ exp $(-67{,}800/RT)$ cm$^2$/sec and $D_{Pu} = 12.4 \times 10^{-5}$ exp $(-64{,}900/RT)$ cm$^2$/sec. Similar investigations carried out at Harwell[32] on mechanically blended powders showed $PuO_2$-rich areas to be 20 to 40 $\mu$ after the first sintering at 1550°C in $CO_2$ and 10 to 15 $\mu$ after a second milling and sintering step. British investigators[33] have also developed a direct alpha-spectrometric technique to examine fabricated and irradiated fuel materials. The advantage of this system is its ability to separate the contribution by various alpha emitters.

The thermal diffusivity and thermal conductivity of $UO_2$–20 $PuO_2$ as a function of temperature and stoichiometry have been measured by the French.[34] The effect of oxygen content is greatest in the lower temperature range (100 to 1000°C) and indicates that the conductivity decreases as the O/M ratio decreases. The most drastic shift in thermal conductivity is accompanied by a decrease in stoichiometry from 2.00 to 1.98. Battelle–Northwest[35a] has also investigated these properties for $UO_2$–25 $PuO_2$. The same general trend but a more gradual decrease with respect to oxygen content was reported. In addition, the mixed-oxide composition with an O/M of 1.97 exhibited good compatibility characteristics with 304 stainless steel after 1000 hr at 650 and 1000°C in either helium- or sodium-bonded assemblies.

Argonne[36] has utilized the Förster resonance technique to establish room-temperature elastic and inelastic properties for $UO_2$–20 $PuO_2$ (O/M = 1.98). Within the density range studied (80 to 85% of theoretical), the Young's modulus and the shear modulus appeared to be linearly dependent upon density. The Young's modulus ranged from 1250 to 1500 kbars, and the shear modulus ranged from 450 to 600 kbars. Los Alamos[14b] has determined the heat of fusion for $UO_2$–20 $PuO_2$ (O/M = 1.97) to be 19.4 kcal/mole by differential-thermal-analysis techniques. The solidus and liquidus temperatures were observed at 2780 and 2820°C, respectively.

Battelle–Northwest[37] has studied the effects of stoichiometry (O/M = 2.00, 1.99, 1.97, and 1.94) on the melting heat rating of $UO_2$–25 $PuO_2$. In the hypostoichiometric region the melting heat rating decreased by 3.2% for an O/M of 1.99 and by 5.5% for an O/M of 1.94. The insensitivity of relative heat rating to decreasing O/M is consistent with a decrease in thermal conductivity and a compensating increase in melting point. General Electric[38] has determined the

melting points of irradiated mixed oxides. The melting point of $UO_2-25\ PuO_2$ after 85,000 Mwd/metric ton decreased 50°C and that of $UO_2-20\ PuO_2$ after 55,000 Mwd/metric ton decreased 100°C. The $UO_2-25\ PuO_2$ irradiated to 250,000 Mwd/metric ton indicated a temperature decrease of 60°C. A decrease in the melting point of 50°C was reported to decrease the effective thermal conductivity ($\int k d\theta$) to melting by ~0.5 watt/cm. Also, the transient-failure threshold for irradiated $UO_2-28\ PuO_2$ fuel after burnup to 70,000 Mwd/metric ton was identified[39] at approximately 50 vol.% molten fuel. The primary mechanism for failure was specified as internal pressure caused by the sudden local release of contained fission gases during the excursion.

Harwell[40] has conducted sintering studies on the $ThO_2-PuO_2$ system. Sintering at 1600°C in argon resulted in densities of 94% of theoretical but poor solid-solution formation. Sintering in air or wet hydrogen yielded good solid solution but poor density in the range 85% of theoretical. The British[41] have also compiled the physical properties of various plutonium and mixed compounds.

## Carbides

Argonne[42] has developed a fluidized-bed process for the preparation of UC–15 PuC. Carbide powder of controlled stoichiometry was produced by carburization of hydrided metal or alloy at 750 to 850°C with mixtures of methane and hydrogen. The composition of the carbides from a series of experiments is shown in Table I-4.

Compatibility results for UC–20 PuC with various commercial cladding alloys have been presented by Latimer.[43] With hyperstoichiometric carbide at 800°C, no new phases were observed after 1000 hr with 304 stainless steel or Timken alloys 16–15–6 and 16–25–6. Tests involving alloys having higher nickel contents, such as Incoloy 800, Hastelloy X, and Inconel 625, have shown some reaction with both the mixed monocarbide and sesquicarbide. Reaction layers for (U,Pu)C ranged from 3 to 180 $\mu$ after 1000 hr at 800°C.

Los Alamos[14b] has developed an arc-melting and hydrogen-treatment process to prepare single-phase UC–20 PuC. The monocarbide with a C/(U + Pu) ratio of $0.97 \pm 0.01$ was readily obtained by hydrogen treatment at 850°C. A reaction time of 0.6 hr/g was necessary to remove the initial 3% excess carbon. Melting temperatures of UC–PuC solid solutions in the compositional range up to 50 wt.% PuC were also determined, and the resulting solidus–liquidus relation is shown in Fig. I-5. Neutron-diffraction studies with $Pu_2C_3$ were performed to establish a postulated antiferromagnetic transition at 120°K, but this transition was not experimentally observed. Compatibility results for (U,Pu)C sodium bonded with 316 stainless steel showed that there was no reaction between the fuel and cladding after 1000 hr at 750°C.

**Table I-4 Analysis of (U, 15 Pu)C Prepared by the Metal–Methane Fluidized-Bed Process[42]**

(Conditions: Temperature, 800°C; Pressure, 2 atm; Gas composition, $H_2$–6.2 vol.% $CH_4$)

| Charge weight, g | Product composition | | | |
|---|---|---|---|---|
| | Carbon, wt.% | Oxygen, ppm | Nitrogen, ppm | Hydrogen, ppm |
| 300 | 4.92 | 340 | 1700 | |
| 300 | 5.00 | 260 | 800 | 55 |
| 400 | 4.93* | 190 | 500 | 180 |
| 400 | 4.76* | 320 | 300 | >250 |
| 400 | 4.75* | 270 | 900 | >200 |

*Products treated with hydrogen at 800°C to reduce carbon content.

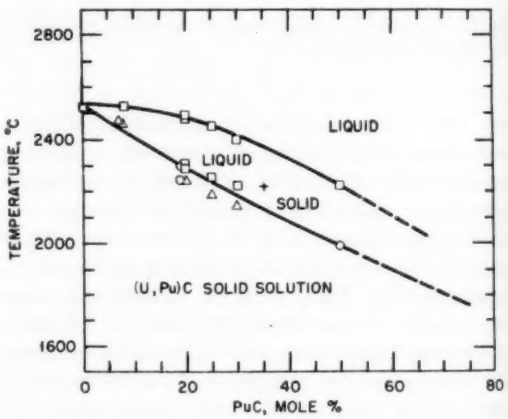


**Fig. I-5 Melting temperatures of UC–PuC solid solutions.[14b] (M/C ratio = 0.95 – 1.00.) ○, metallographic observations; DTA observations: △, arc-melted samples; □, pellets.**

Atomics International[44] has investigated plutonium losses during arc melting of UC–20 PuC. These losses were calculated as a function of the blanket atmosphere and the melt geometry. Los Alamos[45] has also compiled a survey of the properties and irradiation behavior of carbide fuels.

### Nitrides

A study of mixed nitrides (UN–20 PuN) for fast reactor application has continued at Battelle–Columbus.[46] Vapor-pressure determinations for the mixed nitrides indicated that the activity of plutonium is 0.2, and it does not appear to be dependent upon temperature. For PuN the heat of formation was −76 kcal/mole. A $\Delta H^{\circ}_{298}$ of 158.6 kcal/mole was obtained for the reaction $PuN = Pu(g) + \frac{1}{2}N_2(g)$. The plutonium partial pressure for the mixed nitride and PuN is shown in Fig. I-6. Compatibility studies with slightly hyperstoichiometric UN–20 PuN have indicated no reaction between the high-density fuel pellets and 304 stainless steel after 10,000 hr at 700 and 800°C. Compatibility results for 316 and Oak Ridge stainless steel, Inconel 625, Incoloy 800, and vanadium were also obtained. Helium- and sodium-bonded specimens were irradiated to burnups in the range 34,000 to 55,000 Mwd/metric ton, and the observed swelling rates (4.2 to 9.6 vol.%) indicate that a 10-mil gap is sufficient to accommodate fuel swelling to burnups well in excess of 100,000 Mwd/metric ton. Stoichiometric (U,Pu)C was also prepared in this study in a conventional arc melter under 1-atm nitrogen pressure. The carbon concentration in these materials ranged from 3.15 to 3.50 wt.%.

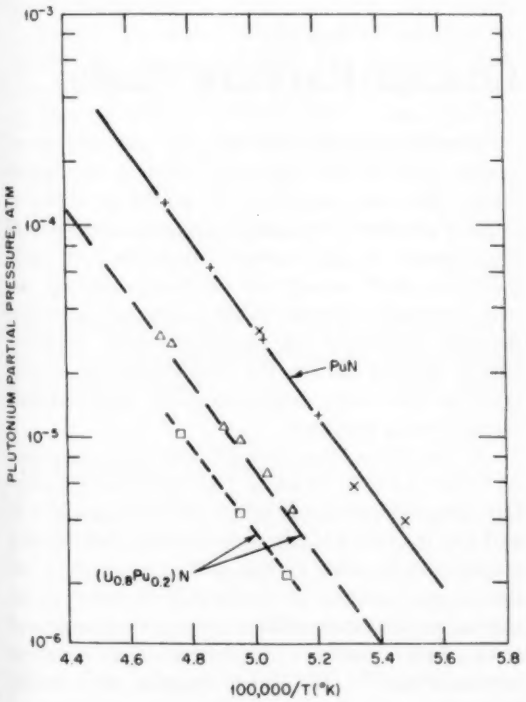


**Fig. I-6 Vapor pressure of PuN and $(U_{0.8}Pu_{0.2})N$ samples.[46] △, 1-mm-diameter orifice; □, 2-mm-diameter orifice.**

Los Alamos[14b] determined the thermodynamic properties of PuN by galvanostatic and mass-spectrometric techniques. The emf from a cell consisting of PuN(s), Pu(s,l)/$PuCl_3$, LiCl–KCl/PuN(s), and $N_2$(g) was measured over the temperature range 680 to 1040°C. The Gibbs free energy of formation for PuN was reported as:

$$-\Delta G^{\circ}_T = 73.8 - 0.0225T \text{ kcal/mole}$$

Vapor-pressure results were in good agreement with Battelle–Columbus results for the partial pressure of plutonium over PuN.

Battelle–Northwest[35a] observed that sodium-bonded UN–20 PuN is compatible with 304 stainless after 1000 hr at 1000°C. The parameters were given for a carbothermic process to produce the mixed nitrides from oxides. After sintering to densities in the range 87 to 95% of theoretical, the impurity levels were found to be 1800 to 8900 ppm for oxygen and 1000 to 6000 ppm for carbon. Thermal diffusivity was measured, and a thermal-conductivity relation was established as shown in Fig. I-7. (M. D. Houston)

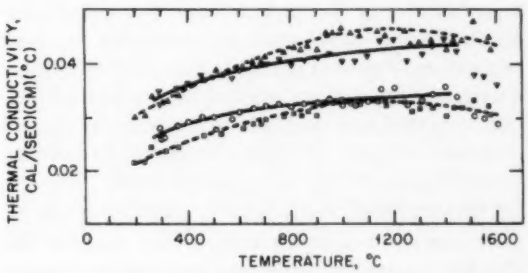


**Fig. I-7 Calculated thermal conductivity of $(U_{0.20}Pu_{0.80})N$ samples.[35a] Metal-hydride (UPu)N: □, 86% theoretical density; △, corrected to 100% theoretical density. Carbothermic (UPu)N: ○, 89% theoretical density: ▽, corrected to 100% theoretical density.**

# Thorium

Battelle–Northwest has irradiated test fuel elements containing a Th–2.5 U (93.2 $^{235}$U)–1.0 Zr alloy in the ETR up to 20,300 Mwd/ton (2.3 at.%) burnup.[35b] After 403 thermal cycles, the fuel has

exhibited 3.8% swelling, as determined by weighing the fuel elements in water. Fuel temperatures were maintained between 350 and 600°C with a surface temperature of 295°C. No evidence of warpage, bowing, or distortion has been noted.

The dependence of the iodide process for refining thorium on the temperature of the crude metal, the deposition temperature, and the pressure of $ThI_4$ vapor has been studied by the Germans.[47] The speed of thorium transport showed a maximum at $ThI_4$ vapor pressure of about 0.06 torr. The occurrence of this transport maximum was attributed to the interplay of the two different transport reactions at the deposition wire. Depending on the total pressure, the speed of the transport is determined by either the phase-boundary reactions on the hot wire or diffusion and convection in the gas phase. (R. L. Martin)

# Metal–Ceramic Fuels

### Dispersion Fuels (Less Than 50 Vol.% Ceramic Phase)

Fuel elements containing powdered $U_3O_8$ or $UAl_3$ dispersed in aluminum powder were fabricated by Oak Ridge[48] for HFIR and ATR applications. These fuel elements were all of the flat-plate type and were manufactured by the picture-frame, hot-rolling technique. Factors that must be controlled in plate fabrication to prevent hot spots and potential melting during reactor operation are fuel loading and distribution, core thickness, quality of heat-transfer bonds, and uniformity of plate curvature. Techniques to optimize these fuel-plate characteristics are discussed.

NASA–Lewis researchers[49] used experimental thermal-strain data obtained by cycling tungsten and W–$UO_2$ composites to determine allowable temperature differences for equivalent thermal strain with a localized temperature perturbation and a uniform temperature gradient in operation. These temperature profiles result in the maximum and minimum thermal strains for typical reactor conditions. The allowable temperature difference for a local temperature perturbation is only one-half that for the uniform gradient.

Idaho Nuclear workers[50] observed that commercially manufactured $U_3O_8$ fuel elements and those manufactured at Oak Ridge have similar performance characteristics. The $U_3O_8$ reaction with aluminum proceeded at a slightly faster rate in the commercial plates. For $UO_2$ and UAl the incorporation of the proper amount and distribution of porosity was found to limit fuel swelling from solid fission products during irradiation. Swelling from fission gas was not observed. (J. T. Smith)

### Cermet Fuels (Over 50 Vol.% Ceramic Phase)

General Electric has fabricated and measured several properties of Mo–$UO_2$ cermets intended for pulse-reactor experiments.[51] Properties that have been measured include sonic velocity, thermal expansion, thermal conductivity, Young's modulus (in compression), and fatigue strength. Cermets containing different fuel loadings and particle sizes were fabricated for testing. The thermal conductivity of a $UO_2$–40 Mo cermet (150-$\mu$ fuel particles) was measured by the radial-heat-flow method, and the data obtained were fitted to the following equation:

$$k = 16.539 + 2.649 \times 10^{-3}\, T$$

where $k$ is the thermal conductivity in Btu/(hr)(ft)(°F) and $T$ is the temperature in °F over the range 750 to 1700°F (400 to 927°C). (R. A. Smith)

# Coated-Particle Fuels

Development of processes for the coating of nuclear fuel particles appears to be at a low rate of effort. However, evaluation of coated products of existing processes is receiving significant attention. At Gulf General Atomic, studies of defective PyC-coated particles, which include an SiC-barrier coating, are being intensified because of the proven significance of defective coatings in fission-product release.[52a] Quantitative information on the contribution of various types of defective coated particles to fission-product release is being obtained.

At Oak Ridge, 20-$\mu$-thick SiC coatings were applied to 14 kg of $ThO_2$ for use in fuel-reprocessing studies. Deposition efficiencies of 60 to 75% and rates of 0.35 to 1.0 $\mu$/min were obtained at 1500 to 1600°C with methyltrichlorosilane as the coating reactant.[53] At Gulf General Atomic, SiC coatings deposited from the coating reactant methyldichlorosilane were compared with SiC coatings deposited from methyltrichlorosilane.[52a] The bend strengths were nearly equal. It was also observed that intergranular pores and cracks were present in the SiC coatings. The frequency of flaws was found to vary between coating runs, and

this could account for the variability in strength of SiC from different coating runs made at nearly identical conditions. (N. D. Veigel)

# Uranium and Thorium Oxides

## Properties and Behavior of Uranium and Thorium Oxides

At General Electric,[54] thermal-conductivity measurements were performed on 82, 86, and 91% dense $UO_2$ at temperatures between 800 and 2000°C in an argon atmosphere by means of the radial-heat-flow technique. The thermal-conductivity values for $UO_2$ to within ±10% were related to the temperature ($T$) and the density ($D$) by the equation

$$k = 0.0130 + \frac{1}{T(0.4848 - 0.4465D)} \text{ watt/(cm)(°C)}$$

for $T$ between 800 and 2000°C and $D$ between 82 and 95% of theoretical.

Henney and Jones[55] employed an optical interferometric technique to study the growth of grain-boundary grooves and the decay of surface scratches on $UO_2$ at 1100 to 1700°C. The surface diffusion coefficient for $UO_{2.005}$ was found to follow the relation

$$D_S = 1.3 \times 10^8 \exp\left[-(110{,}000 \pm 15{,}000)/RT\right] \text{ cm}^2/\text{sec}$$

between 1200 and 1400°C. It was noted that the rate of grooving increased markedly as the oxygen content of the $UO_2$ increased. (R. H. Barnes)

## Preparation of Fuel Bodies

The addition of 0.1 to 4.0 wt.% iridium to $UO_2$ powder to inhibit columnar grain growth at 1800°C is the subject of a U. S. patent.[56] Equiaxed grain growth from 10 to 25 $\mu$ occurred in the iridium-containing specimens, whereas pure $UO_2$ specimens prepared in the same manner exhibited a columnar grain growth about 250 $\mu$ in length with a 40-$\mu$ equiaxed diameter.

A British patent[57] describes the preparation of hollow spherical $UO_2$ particles. The starting $UO_2$ powder is first oxidized at 180 to 300°C, mixed with a small amount of $CaO$–$TiO_2$ powder, granulated, and spheroidized in an oxyacetylene flame at 3000°C. Upon cooling, the spheroids are reduced to stoichiometric proportion in hydrogen. The resultant particles are characterized by high density and closed internal porosity. (T. R. Wright)

# Carbide and Nitride Fuels

## Properties and Behavior

The quasi-ternary systems UC–ZrC–"CeC" and UN–ZrN–CeN have been examined by Holleck and Wagner at several temperatures.[1b,58] The tentative sections obtained at 1400, 1500, and 2000°C are shown in Figs. I-8 and I-9, respectively.

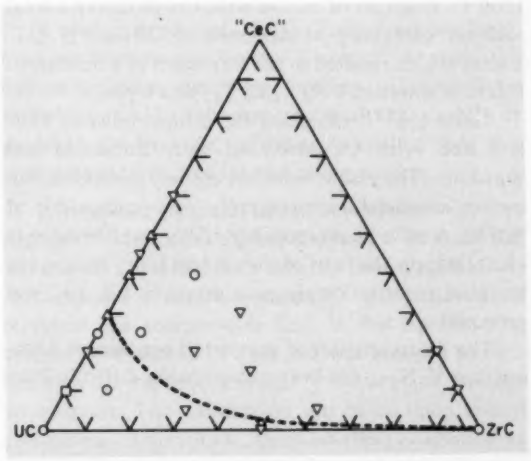


**Fig. I-8 Tentative section of the UC–ZrC–"CeC" diagram[58] at 1400 and 1500°C. Single-phase structure: □, 1400°C; ○, 1500°C. Two-phase structure: △, 1400°C; ▽, 1500°C.**

The Germans[59] have studied alloy formation in UN systems with TiN, HfN, and ZrN. Complete solubility between UN and ZrN was confirmed. Complete solubility between UN and HfN was also observed at 2000°C. The solubility of TiN in UN was found to be 1 mole % at 1700°C, 2 mole % at 2000°C, and 4 mole % at 2400°C.

The reactions of nonmetallic compounds of uranium were investigated by Imoto et al.[1c] The solubility of UB in UN was estimated to be about 12 mole % at

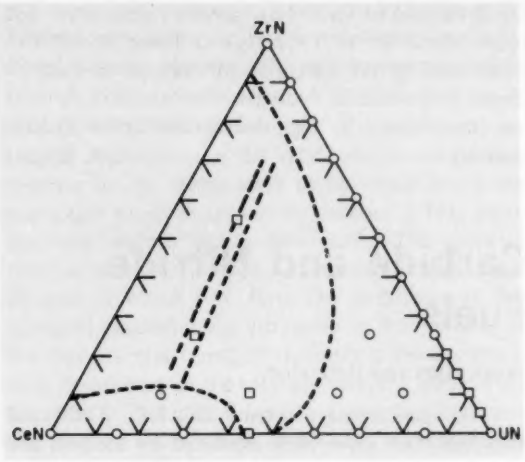


**Fig. I-9 Tentative section for the UN–ZrN–CeN system[58] at 2000°C. ○, single-phase structure; □, two-phase structure.**

1500°C. Reaction of silicon with UN produced a solid solution containing a maximum of 28 mole % USi. Excess silicon resulted in the formation of a mixture of this solid solution, $UN_{0.72}Si_{0.28}$, plus $U_3Si_5$.

Gorle et al.[1d] examined the compatibility of stainless steel with UC stabilized with chromium and vanadium. The results were not entirely consistent, but certain combinations apparently were compatible at 800°C. A new phase, possibly $UVC_2$, was tentatively identified; on the basis of the compatibility results, the tentative constitution diagram shown in Fig. I-10 was proposed.

The determination of the partial pressure of nitrogen over $U_2N_{3+x}$ has been exceptionally difficult. Two

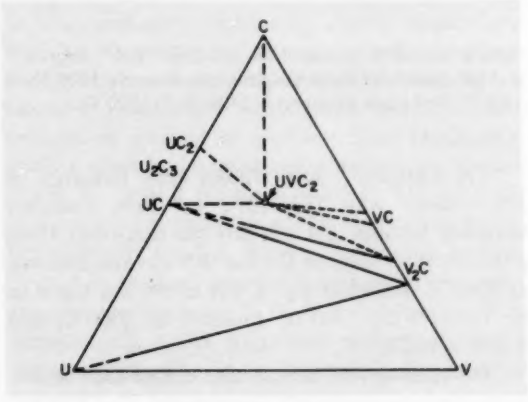


**Fig. I-10 Proposed U–C–V phase diagram.[1d]**

independent investigations of this pressure have succeeded in widening the range of scatter of data already in the literature.[1e,60] This discrepancy may be due to variation of the exact composition of the samples.

Naoumidis and Stöcker[1f] heated UC under nitrogen at atmospheric pressure to obtain a mixture of $UC_{0.02}N_{0.98}$ and graphite. Without removing the graphite, the pressure was then reduced and the mixture heated to equilibrium at various temperatures and pressures to determine the stability of UC–UN solid solutions. It was assumed that the $UC_{0.02}N_{0.98}$ proceeded to equilibrium by the reaction $UC_{0.02}N_{0.98} \rightarrow U(C,N) + N_2$ and that no U(C,N) reacted with carbon to form $UC_2$ or $U_2C_3$. Since such back reactions to form $UC_2$ or $U_2C_3$ are possible and since the pressures obtained were more than an order of magnitude higher than theoretical estimates, it seems likely that the U(C,N) compositions formed at equilibrium contained less uranium and more nitrogen than assumed.

The elastic constants of single crystals of UN were determined by an ultrasonic-vibration method at room

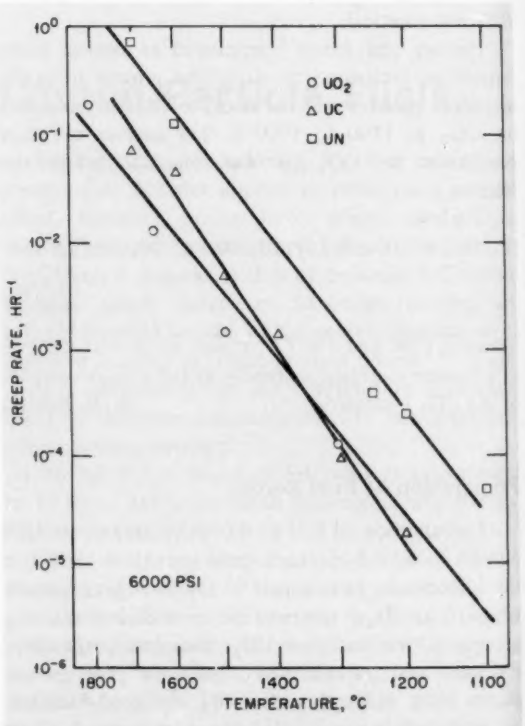


**Fig. I-11 Creep rates of ceramic fuels[62] as a function of temperature at 6000 psi.**

temperature.[61] Young's modulus was found to be $38.4 \times 10^6$ psi; the shear modulus was $15.1 \times 10^6$ psi; and Poisson's ratio was 0.27.

The compressive creep behavior of UC has been examined[62] at temperatures from 1200 to 1600°C and at stresses from 3000 to 10,000 psi. The equation that best fits all the data over this range is:

$$\dot{\epsilon} = 1.8 \times 10^{-3}\ \sigma^3 \exp(-90{,}000/RT)$$

A comparison of these data for UC at 6000 psi with data in the literature for UN and $UO_2$ at 6000 psi shows a remarkable correlation (Fig. I-11). Since these uranium compounds all have cubic crystal structures and since diffusion of uranium probably controls creep by the vacancy mechanism, such a correlation may be expected. (W. Chubb)

### Preparation and Fabrication

Gorle et al.[1g] investigated the reduction of pressed pellets of hyperstoichiometric UC to the single-phase monocarbide by heat-treating in a reducing hydrogen atmosphere. The reduction in pure hydrogen, $UC_2 + 2H_2 \rightarrow UC + CH_4$, starts around 300°C and is very rapid at 550°C. However, reduction of the monocarbide also occurs, $UC + 2H_2 \rightarrow U + CH_4$, and proceeds so rapidly that it is difficult to stop the reaction before formation of a hypostoichiometric product. Diluting the hydrogen with argon reduces the reaction rate considerably and offers the possibility for a controllable commercial process.

The inclusion of methane ($CH_4$) in the hydrogen atmosphere at a concentration intermediate to that required for equilibrium of the two reactions appears more promising. It was shown that a $CH_4$ concentration of 5000 to 8000 ppm (by volume) produced single-phase UC, with the reaction rate practically independent of the concentration. Residual oxygen in the compound can promote the formation of free uranium during subsequent fabrication; therefore both the oxygen content and the fabrication process must be considered in determining the optimum gas mixture.

Single-phase, high-density UC has been fabricated by warm-pressing a stoichiometric mixture of $UC_2$ and uranium powders at 1000°C to obtain a density roughly equal to that of the monocarbide and then reactive sintering at temperatures as low as 1400°C for 2 hr to form the monocarbide.[63] A density of 98% of theoretical is easily attained by this procedure, but further work is required to optimize the parameters of the process. (J. T. Lowder)

# Basic Studies of Irradiation Effects in Fuel Materials

## Metals

Computer analyses can be effective in dealing with some of the complex problems associated with radiation damage in crystals. Klimenkov, Kirsanov, and Osipova[64] conducted a study in which one of the techniques reduces to an examination of a small region in an infinite crystal around the initial location of a primary displaced atom. The remainder of the crystal is replaced by an elastic continuum, and the motion of the atoms in this crystal region is described by classical equations. The size assigned to the region and its shape are determined by the energy of the displaced atom, the computer memory capacity, and the basic content of the problem to be solved.

A computer program, FIGS (Fission Gas Swelling), has been developed at General Electric[65] to study the high-temperature fission-gas swelling of matrix-type fuel elements. The Foreman-type analytical model was modified for this use, providing a method that is a conservative technique for estimating swelling.

A computer program, BEMOD, has been written at Argonne[19c] to model the behavior and to estimate the lifetime of a metallic fuel element during irradiation. An empirical "equation of state" was assumed to represent the compressible fuel. In this equation the volume of a section of fuel rod was assumed to be a function of burnup, ambient pressure, and average temperature. This assumption was based upon several parameters determined from swelling experiments made under pressure. The BEMOD code is being used to compare the predicted behavior of a fuel element with actual behavior in order to determine the adequacy of the code in describing the behavior of the cladding, fuel, and fuel element.

Computer simulations of radiation-damage events in a lead iodide crystal have been carried out by Torrens and Chadderton.[66a] Calculations were restricted to one plane of the lattice, and emphasis was placed on obtaining a qualitative model for the behavior of knocked-on atoms of energies which might result from secondary fission-fragment damage, rather than on accurate quantitative results. In particular, the importance of directional events such as focusing and channeling was investigated.

The damage produced in a single crystal by the excited electrons energized by a fission fragment has been described by Chadderton et al.[66b] on the basis of a simple classical model. An "average" primary electron, or delta particle, possesses a typical energy of some 80 ev which is communicated to the lattice, first by electron–electron interactions and then by electron–phonon interactions. It was concluded that the nature of the fission-fragment damage observed in crystals by electron microscopy will depend primarily upon (1) the rate at which secondary electrons are produced by primaries, (2) the effective range of the secondaries, (3) the activation energies for defect-creating processes, (4) whether the crystal is an element or compound, and (5) the activation energy for defect migration.

Lidiard and Nelson[67] have noted that a strain field generally exists around gas bubbles even in thermodynamic equilibrium. The existence of this strain field leads to a small attraction between bubbles, but, in typical practical situations, this effect is significant for bubble migration only when the bubbles are close together compared to their radii.

In metals irradiated at low temperatures and subsequently subjected to high-temperature treatment, the resulting defects involve the formation of three-dimensional clusters of vacancies (i.e., cavities or pores). This formation is due to the heat-induced relaxation of the local shear stresses that had been generated in the crystal by previous irradiation. A mathematical formulation of this problem has been developed by Lyubov and Semenov[68] regarding the metal crystal as a continuum obeying the macroscopic theory. The macroscopic defects (pores) occur only at high temperatures, and they influence the strength characteristics of the material by restricting, in particular, the migration of dislocations.

The relation between grain-boundary migration and the distribution of inert gas in aluminum has been investigated by Kawasaki.[69] It was concluded that, under the given experimental conditions, the sweeping of inert gases by moving grain boundaries did not have a significant effect. It was not clear in this study whether inert-gas bubbles were formed or not.

## Ceramics

An analytical study of pore migration in ceramic fuel elements has been conducted by Nichols.[70] For the case in which the dominant mechanism of material transport is evaporation–condensation, it was shown that a spherical pore migrates up a thermal gradient without distortion. A second-order effect predicts distortion of an initially spherical shape, the pore tending to elongate along the thermal gradient. Some speculations concerning the origin and stability of the lenticular voids sometimes observed were also reviewed.

The release of fission products from coated fuel particles is being evaluated at Gulf General Atomic.[52b] Estimation of fission-product release has been attempted using the SLIDER code. This code consists of a numerical solution of Fick's law in spherical coordinates, continuity equations, a representation of fission-product decay and birth rates as a function of position, and a thermodynamic description of fission-product behavior at interfaces. These studies are related to safety evaluation of an HTGR-reactor system.

Carroll, Sisman, and Perez[71] have shown that, at relatively high fission densities, the fission-gas release from $UO_2$ is accelerated as the fission density is increased. It was noted that most $UO_2$-fueled, water-cooled power reactors operate in fission-density regions in which the fractional fission-gas release rate is decreasing or is constant with an increase in fission rate. However, some gas-cooled and fast sodium-cooled reactors are planned for operation in the region in which fractional release will increase with higher fission densities.

The microstructures of irradiated $UO_2$ fuel pellets have been examined by Manley[72] using transmission electron microscopy. He observed, for example, that gas bubbles were often associated with black dots that were probably solid fission products. Bubbles not associated with black dots were found to migrate by a surface diffusion process. Evidence that a fission-gas re-solution process must operate during irradiation was also found.

Samples of $UO_2$ and UC were irradiated by Kingery et al.[73] at liquid-nitrogen temperature and then annealed at either 21 or 400°C. Density changes during these anneals were measured to high precision and compared with the corresponding changes in lattice parameter determined by others. For $UO_2$ irradiated to $0.86 \times 10^{16}$ fissions/cm$^3$, the density changes determined by the two methods were in agreement, but, at $0.83 \times 10^{17}$ fissions/cm$^3$, the density decrease measured directly exceeded that calculated from parameter changes. It was concluded that interstitials produced by fission damage recombine to form dislocation loops.

The effect of the migration of fission products on measurements of burnup in fuel elements has been

studied by Miller, Demidov, and Galakhmatova.[74] Migration of fission products along the length of a fuel element was demonstrated using a gamma spectrometer with a Ge–Li detector. It appears that this technique may also give information regarding operating temperatures and the state of the fuel without destroying the fuel element.

In radioactive substances under the effect of their own radiation, point defects of structure (vacancies and interstitial atoms) occur in concentrations considerably higher than they do when the substances are in thermodynamic equilibrium. The energy of these structural defects ("stored" energy) increases the free energy of the irradiated substance, which may cause a change in some of its physical and chemical properties. Gagarinskii, Khripin, and Polishchuk,[75] investigated a method for the thermal analysis of the accumulation of structural defects in the tetraiodide of $^{233}U$ under the effect of self-irradiation. Influences on the temperature of the phase transition were also evaluated.

The processes of radiation damage in ceramic materials of interest in nuclear technology have been reviewed by Lidiard.[76] The growth of gas bubbles in nuclear fuels is one of the topics discussed.

(A. J. Markworth)

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Section

II

Reactor Materials

# Moderator and Control Materials

## Graphite

The fluctuations in area density over a disk of high-density graphite 45 mm in diameter and 14 mm thick were measured by the British[1] using a 147-Mev proton beam as the nondestructive probe. An accuracy of ±0.08 kg/m$^2$ at each point and a spatial resolution of 3 mm were reported. The technique is considered capable of giving an accuracy of ±0.003 kg/m$^2$ or ~1% of the value of fluctuation, whichever is greater, and a spatial resolution of less than 1 mm for samples up to 100 to 200 kg/m$^2$ thick.

Information on carbon-base materials for superheat service in reactor cores was compiled by Canadian researchers.[2] It was noted that the present electrographites do not meet the requirements for this application without improvements in such properties as fracture toughness and oxidation resistance.

The oxidation of a variety of PyC (pyrolytic carbon)-coated fuel-particle types by water vapor has been investigated at Oak Ridge.[3] Flowing He–$H_2O$ mixtures having water-vapor concentrations of 250 to 1000 ppm and a total pressure of 1 atm were studied at 1100 to 1400°C. Rates of reaction of water vapor with PyC coatings were determined from continuously recorded weight changes and from analysis of effluent gases for reaction products. The extent of coating failure was determined from the quantity of uranium and/or thorium leached by acid from the oxidized fuel particles. Differences in oxidation rates were observed for the various batches of coated particles which could not be correlated satisfactorily with the density, anisotropy, and crystallite size of the coatings. Percentages of failed coatings at constant burnoff also varied from batch to batch.

Diffusion data for Cs, Sr, Ba, and Eu in PyC were reviewed by Gulf General Atomic.[4] A linear relation between diffusion coefficients and atomic radii of the metals was suggested by the results as illustrated in Fig. II-1. All the diffusion experiments were carried out using either metal chloride or oxide sources. Since it was shown that the diffusion coefficients for cesium in PyC were higher with a $Cs_2O$ source than with a CsCl source, the question exists as to how well the data apply to reactor calculations where the diffusion sources could be expected to be the metals or metal carbides.

The Japanese[5] have investigated the effects of irradiation on hard carbons (such as the low-permeability glassy carbons). The radiation contraction of hard carbon was found to be isotropic and nonannealable, and X-ray diffractions of the material indicated changes similar to graphitization without high-temperature heat-treatment. The permeability of reactor graphite impregnated with hard carbon was observed to increase with irradiation.

A pressure cell with a resistance-heated graphite test specimen in a helium atmosphere was used to determine the triple point of four grades of graphite[6]

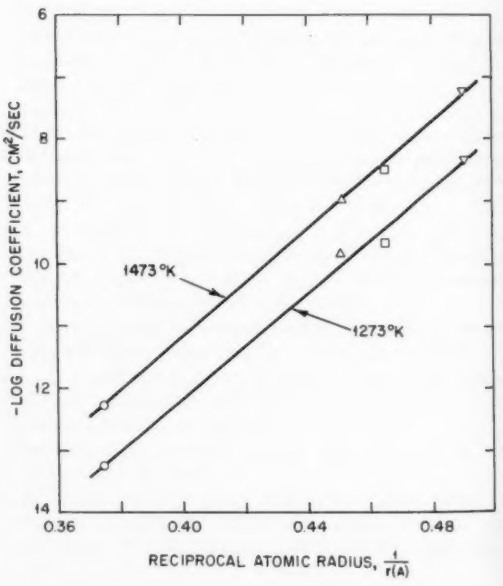


**Fig. II-1 Comparison of calculated and measured diffusion coefficients for transport in isotropic pyrocarbon.[4] —, calculated; measured: ○, Cs data; △, Ba data; □, Sr data; ▽, Eu data.**

to 1000 atm abs. The triple-point pressure was determined to be 103 atm for all four grades. The temperature varied for each grade as follows: 7529 ± 19°R for AGOT, 7606 ± 60°R for LANG, 7629 ± 30°R for AGSR, and 7738 ± 45°R for AGKS. The solidus–liquidus interface from the triple point to 1000 atm was also experimentally determined for the LANG graphite. The melting point increased with increasing pressure from 7645°R at 103 atm to 7750°R at 1000 atm.

The increasing importance of nondestructive testing of graphites is reflected in an ASTM publication[7] that presents the papers on nondestructive testing of nuclear graphite from a symposium held in June 1967.

Experiments and analyses to establish the power-density and thermal-stress limitation of graphite fuel elements in Rover reactor cores have been summarized.[8] Significant experimental improvements, modifications, and advances in analytical techniques were noted. The effect of temperature on the correlation between the calculated stress and the experimental data at fracture was also established. (M. C. Brockway)

# Beryllium and Beryllium Alloys

## Mechanical Metallurgy

### Divergent X-Ray Beam Studies

The ductile–brittle behavior of beryllium is being studied at Rutgers[9] by characterizing the slip activity and substructural changes which lead to room-temperature cleavage failure and the substructure induced by deformation at higher temperatures. A divergent X-ray beam apparatus was used to obtain the strain configurations in single crystals. Changes in the deficiency conics in the forward-transmission region provided a measure of the substructural changes induced by deformation. When the conic sections of the Kossel-type patterns were sharp and continuous, the crystal was relatively free of defects. Broadening, diffuseness, or discontinuities in the curves indicated the development of a defect structure in the crystal. Also, variations in background intensity allowed foreign particles 1 $\mu$ or less in diameter to be observed. Compression specimens oriented for basal slip indicated the formation of tilt and twist boundaries in the early stages of deformation. Reversing the slip direction by rotating the compression specimen resulted in partial restoration of some deformed regions.

### Flow Stress for Prism Slip

The flow and fracture characteristics of zone-purified beryllium and beryllium-rich alloys were studied by London and Damiano.[10] Single-crystal-deformation studies of prism slip on zone-refined (12-pass) material and on a 0.68 wt.% copper alloy indicated a flow-stress temperature inversion from 25 to −150°C, with a lower flow stress being observed at the lower temperature. Slip-trace observations suggested that the character of the slip process changed so that prism glide was facilitated at the lower temperatures. Transmission-electron microscopy showed that, as the temperature was lowered from 25 to −150°C, the frequency of thermally activated cross slip from the prism to the basal plane decreased. Thus the normally measured flow stress for prism slip in beryllium at room temperature is anomalously high because of rapid work hardening resulting from the thermally activated cross-slip process.

### Beryllium Brittleness

Franklin Institute has continued to investigate factors relating to the brittleness of beryllium.[11] The studies are divided into three relatively distinct phases: (1) bicrystal and related behavior, (2) prestraining effects, and (3) theoretical analysis relating to the mechanical behavior of beryllium.

Bicrystal tests have been performed at temperatures up to 350°C on specimens that exhibited little ductility at room temperature. Although macroscopic compatibility can be satisfied in beryllium bicrystals, failure by cleavage on the (0001) plane or $(1\bar{1}20)$ planes is the result of a crack-nucleation mechanism at bend planes arising after some plastic flow. The crack leading to failure then continues by rapid propagation under the influence of a large normal stress. Room-temperature tensile tests on textured polycrystalline material revealed that cracks originate at bend planes for which the normal stress (0001) plane was greatest. It was suggested that the increased ductility with temperature of the bicrystals is associated with the blunting of the (0001) and $(11\bar{2}0)$ cracks, possibly by local pyramidal slip. Polycrystalline samples that also exhibited increased ductility at temperatures of 200 to 350°C were found to contain cracks that do not readily propagate, suggesting a similar blunting mechanism.

Elastic constants of beryllium and its alloys were calculated from the theory of the electronic structure of metal. Using Gilman's expression for the surface energy and calculating the value of the alpha parameter

(representing the range or relaxation distance of the atomic forces) for the various crystallographic planes, the surface-energy value obtained for the (0001) plane was lower than that for the $(10\bar{1}0)$ plane. These results agree with experimental observation but are in contrast to the lower value of the surface energy for the $(10\bar{1}0)$ planes obtained by Gilman.

A theory developed by Armstrong[12] for the ductile-to-brittle transition in hexagonal close-packed metals has been applied to limited tensile data on beryllium. The ductile–brittle behavior was related to the critical resolved shear stress for the various deformation systems in single crystals. The theory predicts that at small grain sizes

$$T_c = A + Bd^{-\frac{1}{2}}$$

where $T_c$ is the transition temperature, $d$ is the average grain diameter, and $A$ and $B$ are constants that depend on the material. These constants are determined by the following parameters:

1. Preferred orientation.
2. Fracture characteristic of the material.
3. Slip process within the grains.
4. Accommodating plastic flow mechanism at the grain boundaries.

### Fracture Toughness

The influence of loading rate and testing temperature on the fracture toughness of AMS-7902 beryllium sheet has been studied at Boeing.[13] Center-crack and semielliptical part-through crack specimens were tested at variable stress rates. The results of these tests are presented in Fig. II-2. Cyclic tensile loading tests were also performed with center-crack specimens at a constant frequency of 30 cps. These tests appear to support the Corten–Shoemaker hypothesis that an Arrhenius-type relation exists among strain rate ($\dot{\epsilon}y$), frequency factor ($A$), absolute temperature ($T_R$), and fracture toughness ($K_{Ic}$). Only large changes in loading rate had an appreciable effect on $K_{Ic}$. For severe stress environments, a minimum $K_{Ic}$ was found which was relatively insensitive to further reduction in testing temperature and increases in stress rate. This minimum of 11 ksi$\sqrt{\text{in.}}$ is recommended as a design $K_{Ic}$ value.

## Physical Metallurgy

Recovery and recrystallization studies of beryllium sheet with additions of 3.3 wt.% copper or 4.2 wt.% nickel were performed at Franklin Institute.[10] The

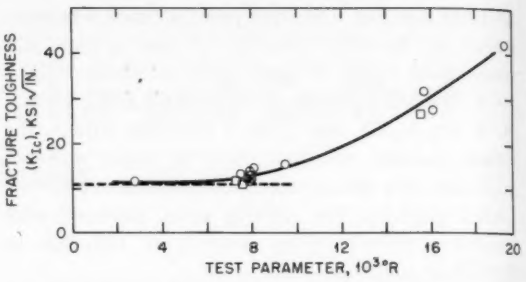


**Fig. II-2 Effect of temperature and strain rate on fracture toughness of AMS-7902 beryllium.[13] ○, center-crack specimens; □, surface part-through specimens. $P$ (parameter) = $T_R$ ln $(A/\dot{\epsilon}_y)$, where $T_R$ is absolute temperature, °R; $A$ is frequency factor, $10^3$ sec$^{-1}$; and $\dot{\epsilon}_y$ is strain rate in $y$ direction, sec$^{-1}$.**

optical microstructure of specimens heat-treated in the 600 to 650°C range exhibited very little change, whereas a heat-treatment of 700°C for 15 min produced recrystallization. Transmission-electron microscopy revealed that a wide range of substructures was produced in the recovery heat-treatment range of 600 and 650°C even though the optical microstructure failed to reveal significant responses. Bend and tensile tests showed that the greatest ductility was observed for recovered rather than recrystallized material and that recrystallization also caused a decrease in strength. Thus, for improved mechanical properties, it appears to be preferable to heat-treat beryllium in the recovery range rather than at recrystallization temperatures.

The Russians[14] investigated self-diffusion in polycrystalline beryllium by using the $^7$Be isotope. Curves were constructed of the specific activity as a function of the diffusion quadratic for temperatures of 650, 800, 900, 1000, and 1200°C. The diffusion coefficient as a function of temperature was calculated to be

$$D = 0.36 \exp(-38{,}400/RT) \text{ cm}^2/\text{sec}$$

## Powder Metallurgy

The effects of powder particle size on the physical behavior of press-forged beryllium have been investigated by the Army.[15] A single lot of electrolytic beryllium powder was sized to fractions of nominally −43 $\mu$ and −20 $\mu$. This provided approximately an equivalent metallic-impurity content for the two fractions, with powder-surface area and resulting oxide distribution in the densified beryllium being the main variables. The total oxide content was similar for the two powder fractions (1.0 wt.% oxide for the −43-$\mu$

powder and 2.2 wt.% oxide for the −20-$\mu$ powder). Both powders were vacuum hot pressed to block, and 2-in. cubes were machined for press forging to a ½-in. height. Prior to forging, the specimens were solutionized at 1900°F (1040°C) for 6 hr and quenched in flowing argon.

After forging at 1400, 1600, 1800, and 1900°F (760, 870, 980, and 1040°C), specimens were either aged at 1400°F for 8 hr and furnace cooled or solutionized at 1900°F for 6 hr and quenched in flowing argon. The impact strength, as shown in Fig. II-3, was influenced by powder particle size; the −20-$\mu$ material exhibited a resistance to impact considerably greater than that exhibited by the −43-$\mu$ material. Forging or heat-treatment at the higher temperatures substantially decreased these effects. The tensile strengths, as shown in Fig. II-4, have similar trends but to a lesser extent. Metallographic examination of samples produced with both powder sizes revealed little difference in that all exhibited similar grain sizes and the oxide particles were concentrated in network-like zones. Thus the oxide dispersoid appears to influence beryllium beyond the normally considered grain-refinement strengthening.

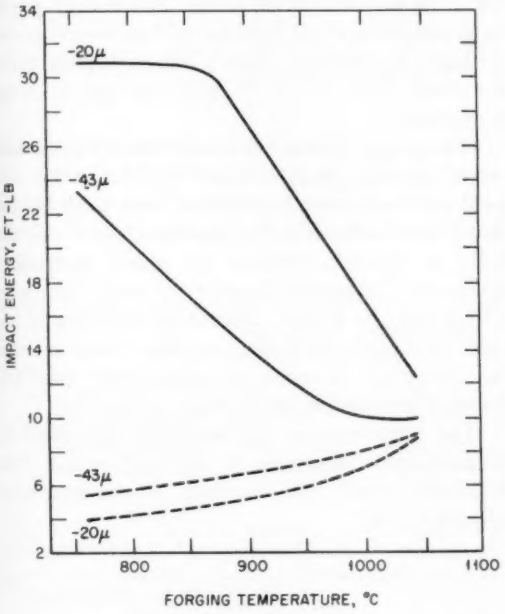


**Fig. II-3 Impact resistance of forged-beryllium powder block.[15] —, 1400°F treatment; - - -, 1900°F treatment.**

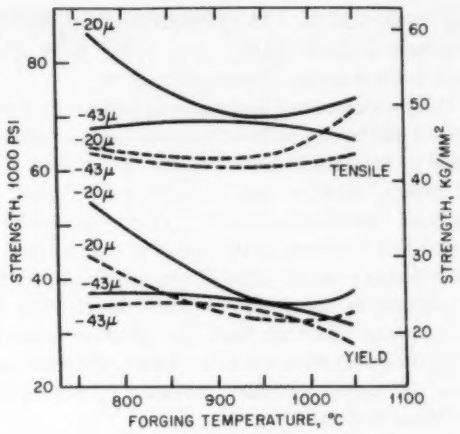


**Fig. II-4 Yield and tensile strength of forged-beryllium powder block.[15] —, 1400°F treatment; - - -, 1900°F treatment.**

## Corrosion

Corrosion of beryllium by water vapor (5 and 30 mm Hg) at 600 to 800°C was studied with a Gulbransen-type microbalance.[16] At 600°C, oxidation followed the parabolic rate law during an initial period, after which the pattern became exponential. At 650 and 700°C the oxidation at first proceeded exponentially and later became linear with time. The latter step was accompanied by breakaway of the oxide film. At 800°C the oxidation obeyed the rectilinear rate law throughout the course of the experiment. Electron metallography indicated that the logarithmic-rate behavior can be attributed to the generation of blisters at the oxide–metal interface and that the ensuing rectilinear pattern stems from breakaway of the oxide film. (F. T. Zurey)

# Solid Hydrides

## Hydrided Zr–U Alloys

Pressure–temperature isochores for the Zr–U–H system have been extended to 1300°C in measurements at Gulf General Atomic.[17] The compositions covered the H/Zr range from 1.50 to 1.70 with a uranium content of 8 wt.% for most of the work, although some data were obtained for the pure ZrH. Equilibrium dissociation pressures at high temperatures for H/Zr compositions from 1.60 to 1.70 agreed with values extrapolated from data previously determined for temperatures below 900°C. However, for the H/Zr

range from 1.50 to 1.55, the equilibrium pressures at temperatures above 1000°C were found to be significantly lower than the extrapolated values.

Fully enriched test fuel elements containing 8 wt.% uranium and having H/Zr ratios from 1.60 to 1.65 were loaded in the TRIGA Mark F reactor and pulsed. After 400 pulses, selected fuel elements were declad and examined metallographically. These examinations showed that fuel-body performance at temperatures up to the design point of 1000°C was satisfactory in that no evidence of interaction between the cladding and the fuel was observed. Peak gas pressures measured during the pulses were less than 40 psig, which was well below the upper boundary indicated by the equilibrium pressure data.

## Yttrium Hydride

A U. S. patent for a moderator fuel element based on $YH_2$ has been granted to the Atomic Energy Commission of France.[18] The element consists of molybdenum-coated fuel particles dispersed in the $YH_2$ moderator. The fabrication method disclosed requires that ground yttrium metal be mixed with the coated fuel particles and the mixture then sintered. The sintered product is placed in a can of molybdenum or other refractory alloy and then hydrided. A British patent has also been obtained on the process.[19]

## Rare-Earth Hydrides

The light rare-earth metals form a single-phase dihydride that expands without structural change to the trihydride composition as hydrogen is added. However, the heavy rare earths undergo a structural change in going from the dihydride to the trihydride. For this reason a typical heavy rare earth, erbium, has been studied in detail with respect to its hydride phases. At the same time that work was being conducted at Denver Research Institute,[20] Russian investigators[21] were also studying the Er–H system. Pressure–temperature–composition data were obtained at Denver over the composition range from pure metal to $ErH_3$, whereas the Russian investigators used X-ray diffraction techniques to study the same compositions. Both groups used the best erbium metal available, which was 99.9 wt.% in the case of the U. S. investigators and 99.5 wt.% for the Russian workers.

Because the approaches in the two studies were different, and the data are presented differently, it is difficult to compare results. In addition, the X-ray data were taken at room temperature, whereas the isotherms were derived at high temperatures. However, both studies showed that, as hydrogen is absorbed by the hexagonal erbium metal, a face-centered cubic phase characterized as $ErH_2$ is formed. The Russian investigators found a two-phase region, consisting of Er–H solid solution and $ErH_2$, from 7 to 66 at.% hydrogen at room temperature. From 500 to 950°C in the Denver work, this two-phase region appeared in the range 28 to 33 at.% hydrogen and extended to 66 at.% hydrogen. Both groups found a narrow range of homogeneous $ErH_2$ between 66 and 68 at.% hydrogen. Another two-phase region, consisting of $ErH_2$ and $ErH_3$, was located between 68 and 73 at.% hydrogen at room temperature and from 68 to 75 at.% hydrogen at the higher temperatures. Finally, the single-phase $ErH_3$ was noted from 73 to 75 at.% hydrogen at room temperature.

The Russian workers determined the lattice parameter of the $ErH_2$ phase to be $a_0 = 5.125$ A, which is in good agreement with unpublished work cited by the Denver group. However, the Russians claimed that the $ErH_3$ is rhombic, whereas the others reported a hexagonal close-packed structure for $ErH_3$, with $a_0 = 3.63$ A and $c_0 = 6.54$ A. Considering that some of the other rare-earth trihydrides have been found to have the hexagonal structure, it seems likely that the Russians have indexed the structure incorrectly.

The isotherm work also permitted calculation of thermodynamic properties of the Er–H system. The differential heats and entropies of reaction were calculated to be:

| | $Er_{ss} + ErH_2$ | $ErH_2 + ErH_3$ |
|---|---|---|
| Heat of reaction, kcal/mole $H_2$ | $-52.6 \pm 0.3$ | $-19.8 \pm 0.2$ |
| Entropy of reaction, cal/(mole $H_2$)(°C) | $-35.2 \pm 0.3$ | $-30.1 \pm 0.4$ |
| Log dissociation pressure, torrs | $-\frac{11{,}500 \pm 70}{T} + 10.57$ | $-\frac{4320 \pm 50}{T} + 9.46$ |

The integral free energies, enthalpies, and entropies of mixing determined for the Er–H system are shown in Table II-1.

The character of the Er–D system was also established at Denver Research Institute.[22] The only observable difference in the pressure–temperature–composition data was a shift to higher pressures in the deuterium curves compared with the hydrogen curves.

**Table II-1 Integral Free Energies, Enthalpies, and Entropies of Mixing in the Er–H System[20] at 923°K**

| Composition, H/Er ratio | $-\Delta G^M$, kcal/ gram atom soln. | $-\Delta H^M$, kcal/ gram atom soln. | $-\Delta S^M$, cal/ (°K)(gram atom soln.) |
|---|---|---|---|
| 0 | 0 | 0 | 0 |
| 0.05 | 0.71 | 1.05 | 0.37 |
| 0.10 | 1.27 | 2.00 | 0.79 |
| 0.15 | 1.75 | 2.88 | 1.22 |
| 0.20 | 2.19 | 3.70 | 1.64 |
| 0.25 | 2.55 | 4.47 | 2.08 |
| 0.30 | 2.87 | 5.20 | 2.52 |
| 0.35 | 3.17 | 5.91 | 2.96 |
| 0.40 | 3.43 | 6.57 | 3.40 |
| 0.45* | 3.70 | 7.21 | 3.80 |
| 1.80* | 6.10 | 15.60 | 10.30 |

*Solubility boundaries of the two-phase region, $Er_{ss} + ErH_{1.80}$.

The solubility boundaries for the Er–D system were the same as those for the Er–H system, within experimental error. The heats of reaction and entropies of reaction were also very close to those found with hydrogen:

| | $Er_{ss} + ErD_2$ | $ErD_2 + ErD_3$ |
|---|---|---|
| Heat of reaction, kcal/mole $H_2$ | $-53.0 \pm 0.2$ | $-20.0 \pm 0.1$ |
| Entropy of reaction, cal/(mole $H_2$)(°C) | $-36.3 \pm 0.2$ | $-31.0 \pm 0.2$ |
| Log dissociation pressure, torrs | $-\frac{11{,}570 \pm 40}{T} + 10.81$ | $-\frac{4380 \pm 30}{T} + 9.66$ |

The integral values for the thermodynamic quantities involving the Er–D system are presented in Table II-2.

## Ternary Hydrides

Ternary systems with zirconium, hydrogen, and either carbon or nitrogen were studied by Andrievskii et al.[23] Ternary compounds were formed by hydriding ZrC and ZrN at about 1000°C. A wide range of homogeneity was observed, and lattice-parameter values were determined for compositions approximating $ZrC \cdot ZrH_{1.5}$ and up to $ZrC \cdot ZrH_2$; these values were very close to the values $a_0 = 3.3467$ A and $c_0 = 5.4898$ A reported by Atomics International[24] for this hexagonal lattice.

**Table II-2 Integral Free Energies, Enthalpies, and Entropies of Mixing in the Er–D System[22] at 923°K**

| Composition, D/Er ratio | $-\Delta G^M$, kcal/ gram atom soln. | $-\Delta H^M$, kcal/ gram atom soln. | $-\Delta S^M$, cal/ (°K)(gram atom soln.) |
|---|---|---|---|
| 0 | 0 | 0 | 0 |
| 0.05 | 0.68 | 1.02 | 0.37 |
| 0.10 | 1.23 | 1.96 | 0.79 |
| 0.15 | 1.77 | 2.91 | 1.22 |
| 0.20 | 2.00 | 3.52 | 1.65 |
| 0.25 | 2.56 | 4.49 | 2.09 |
| 0.30 | 2.90 | 5.23 | 2.53 |
| 0.35 | 3.19 | 5.94 | 2.98 |
| 0.40 | 3.42 | 6.59 | 3.44 |
| 0.45* | 3.64 | 7.22 | 3.88 |
| 1.80* | 5.87 | 15.80 | 10.78 |

*Solubility boundaries of the two-phase region, $Er_{ss} + ErD_{1.80}$.

With nitrogen, the composition $ZrN_{0.4}H$ was obtained, and the hexagonal lattice constants were $a_0$ = 3.285 A and $c_0$ = 5.470 A. These values are slightly lower than those observed previously in structures with less nitrogen. The Russians also measured the electrical resistivity of both sets of ternary compounds and obtained values of the order of 1000 $\mu$ohm-cm, which indicates that the compounds are defect structures.

(H. H. Krause)

# Metallic Poison Materials

Calhoun and Fascia[25] determined that a minimum of 10% cold work is necessary before grain refinement in hafnium can be obtained by recrystallization. The smallest grain size was obtained by a high degree of cold work followed by low-temperature annealing. The final grain size was primarily dependent on the amount of cold work and to a lesser degree on the working temperature or the annealing temperature. Figure II-5 illustrates the relation between final grain size, cold work, and annealing temperature. Increased oxygen content results in significant hardness increases at lower temperatures, but above 600°C the microhardness of hafnium appeared to be independent of oxygen content.[26]

(M. Kangilaski)

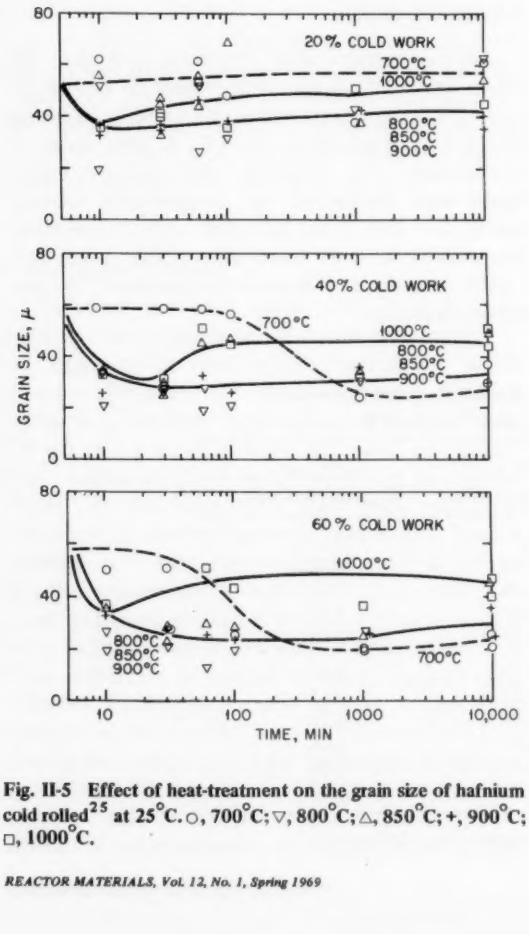


**Fig. II-5 Effect of heat-treatment on the grain size of hafnium cold rolled[25] at 25°C. ○, 700°C; ▽, 800°C; △, 850°C; +, 900°C; □, 1000°C.**

# Dispersions and Nonmetallic Poisons

## Boron and Boron Compounds

Two methods were developed at Oak Ridge[27] which can be used to transform the more readily available low-density amorphous boron to a higher density, high-purity crystalline boron powder. In the first method, amorphous boron-metal powder was placed in high-purity (HPR-grade) boron nitride containers and heated to 2000 to 2150°C in a tungsten-susceptor induction furnace with an argon atmosphere. In the second method the boron-metal powder was passed through a sheath-stabilized helium plasma flame onto a water-cooled target to produce an essentially massive body. Amorphous normal boron as produced by the reduction of the oxide ($B_2O_3$) by magnesium metal was crystallized and purified to greater than 99 wt.% boron by both of these methods. Electrolytic-cell-produced amorphous $^{10}B$ metal powder was crystallized and purified to greater than 97 wt.% boron by both methods.

Mound Laboratory[28] studied the packing characteristics of irregularly shaped crystalline boron particles in the size range 20 to 105 $\mu$. The particles were sized into seven successive groups and revealed many of the same packing characteristics as found for spheres. Maximum densities achieved with these powders were slightly lower than those for spheres and were not consistently repeatable.

Russian workers[29] irradiated various boride samples to determine the effect of lattice damage from the $^{10}B$ isotope in the natural boron. The samples were approximately 8 mm in diameter and 10 to 15 mm long. Irradiation to $10^{20}$ neutrons/cm$^2$ (thermal) at <100°C caused samples of $ZrB_2$, $CrB_2$, and $LaB_6$ to shatter into bits, but merely produced cracks in $TiB_2$ and $(TiCr)B_2$ specimens. The radiation stability of the substance was correlated with the modulus of elasticity. A maximum lattice expansion of 3.1 vol.% was

observed in the case of $TiB_2$, whereas $ZrB_2$ showed a lattice expansion of only 0.9 vol.%.

A British patent[30] claims that the mechanical properties of particles of boron or boron-containing compounds such as $B_4C$ are improved by vapor coating with an inner layer of SiC and an outer layer of TiC by the fluidized-bed process. The coated particles are then dispersed in a metal matrix and fabricated into control elements by conventional techniques.

The shrinkage behavior of $TaB_2$ powder compacts in vacuum at 1100 to 2100°C was examined by investigators at Lockheed.[31] A density of 94% of theoretical was obtained by sintering for ½ hr at 2100°C. It was found that initial-stage sintering occurs by either a volume or grain-boundary diffusion mechanism with an activation energy of approximately 90 kcal/mole. It was also noted that compacts of a powder mixture of $TaB_2$ plus boron in excess of stoichiometry expanded upon sintering.

A review of the properties and reactor performance of boron carbide has been compiled by Battelle–Northwest[32] to assess its potential for fast-reactor application. Data from 34 references concerning the irradiation behavior of $B_4C$ with respect to gas release, swelling, mechanical integrity, and dimensional stability in thermal reactors to 500°F (260°C) and for burnups to 50% of the $^{10}B$ isotope in natural boron were included. It was concluded, however, that realistic performance evaluation of $B_4C$ requires testing in a fast-neutron environment at the temperatures of interest.

### Rare Earths

The $HfO_2$–$Sm_2O_3$ diagram in the solid-phase region rich in $HfO_2$ was investigated by the Russians.[33] The diagram of $HfO_2$–$Sm_2O_3$ was compared with that of $ZrO_2$–$Sm_2O_3$. During the interaction of $HfO_2$ with $Sm_2O_3$, solid solutions are formed with a composition close to 33 mole % $Sm_2O_3$ and 67 mole % $HfO_2$. On further reaction with excess $HfO_2$, equilibrium reaction products were formed. (D. E. Lozier)

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Section III

Reactor Materials

# Cladding and Structural Materials

## Corrosion by Aqueous and Gaseous Media

### Corrosion of Zirconium Alloys

The effect of heat transfer and isothermal conditions on the corrosion and hydriding of Zircaloy-4 tubing in a pressurized-water system has been studied at Westinghouse.[1] Bulk-water temperatures ranged from 600 to 640°F (316 to 338°C), and metal surface temperatures were 20 to 80°F (11 to 44°C) higher. Heat fluxes were 3420 to 13,000 Btu/(hr)(sq ft) under forced-convection conditions and 20,000 Btu/(hr)(sq ft) under nucleate-boiling conditions. The oxidation rate was directly proportional to the cladding surface temperature in all heat-transfer systems studied. Hydrogen absorption was the same in the nucleate-boiling systems as in the forced-convection systems and was homogeneous throughout the tube cross sections. There were no abnormal hydride-platelet clusters in the microstructures.

Knolls researchers[2] have investigated the effect of silicate ions released from spent ion-exchange resins on the high-temperature steam corrosion of Zircaloy. In 14-day tests at 750°F (400°C) in 1500-psi steam, corrosion rates were accelerated for Zircaloy sensitized by slow cooling from 1650°F (900°C) with 0.12 ppm silicon in the water and for reactor-grade Zircaloy with 1.3 ppm silicon in the water.

### Corrosion of Aluminum Alloys

A new accelerated stress-corrosion laboratory test for aluminum alloys has been developed by Kaiser Aluminum and Chemical Corp.[3] The test consists of a 1-week immersion of chemically etched C-ring or round tensile specimens in a 1 NaCl–2 $K_2Cr_2O_7$ (by weight) solution at *p*H 4 and 60°C. The accelerated-test results were correlated with marine and industrial exposures and with the 3.5 NaCl (by weight) alternate-immersion test. Good correlation was obtained for the susceptible tempers of 2014, 2019, and 2024 alloys. However, the outdoor environments were more prone to cause stress-corrosion cracking than was the new accelerated test at the lower stress levels with 7039, 7075-T651, and 7079-T651 alloys.

### Corrosion of Iron-Base Alloys

#### Steel

The oxidation of mild and low-alloy steels at 500°C in $CO_2$ containing small amounts of CO and $H_2O$ has been studied at Harwell.[4] Oxide scales were double layered, and oxygen transport in the nonprotective oxides was believed to be by gas diffusion through open pores. Oxygen transport in the protective oxides was believed to occur across closed pores that formed as the result of the condensation of vacancies produced by cation diffusion through the film. Nonprotective oxidation occurred at high $CO_2$ pressures in the presence of water vapor. The adverse influence of water vapor was enhanced by deposits of gold, platinum, and carbon on the metal surface. These elements appeared to increase oxidation by chemical reaction rather than by mechanical effects in the oxide film.

#### Stainless Steels

The structure and composition of thin films formed on an Fe–15 Cr–4 Al–1 Y* alloy during oxidation in $CO_2$ at 800 to 1000°C have been determined by the British.[5] X-ray diffraction revealed $FeCr_2O_4$ spinel, $Al_2O_3$, and $Y_2O_3$. Neither of the latter two phases appeared to form a solid solution with any other component of the oxide film. Over the exposure period of 0.1 to 1000 hr, the rate-controlling step was attributed to self-diffusion of $Al^{3+}$ in $Al_2O_3$. No other phase contributed significantly to the oxida-

*Unless otherwise designated, all compositions are considered to be in wt.%.

tion behavior of the alloy, except for $Y_2O_3$, which apparently improved scale adhesion.

The oxide-scale formation on superheater alloys exposed up to 36 months in high-temperature steam has been investigated for the ASME.[6] Commercial superheater-tubing specimens were exposed to 2000-psi steam in a large steam-generating plant. Ferritic materials were exposed at 1100 and 1200°F (595 and 650°C), and austenitic materials were exposed at 1200, 1350, and 1500°F (650, 730, and 815°C). A subsurface layer and a surface layer of the oxide scales formed on both grades of materials. Apparently the subsurface layer was formed by inward diffusion of anions of oxygen and the surface layer by the outward diffusion of cations of iron and manganese. The subsurface layer was dense and consisted of oxides of the alloying elements of the base metal. Concentrations of these alloying elements in the subsurface layer were higher than those in the base metal. The surface layer was primarily iron oxide and contained many voids and pores. After an 18-month exposure at 1350°F, the average scale thickness on 310 stainless steel, Incoloy 800, and Inconel 600 was <1.5 mils compared with 4 to 5 mils for most of the other austenitic materials and 15 to 25 mils for the ferritic alloys at 1200°F.

The effectiveness of phosphates in inhibiting stress-corrosion cracking of austenitic stainless steel as related to the N Reactor has been studied at Battelle–Northwest.[7] Autoclave tests were conducted for 8 months in 100-psi water containing 0 to 1000 ppm phosphate, 0 to 100 ppm sulfite, 0 to 15 ppm hydrazine, 2 ppm morpholine, and no added chloride (chloride ranged from <0.05 to 1.84 ppm). After a 4-month exposure, stress-corrosion cracking occurred in 304 stainless-steel tubing taken from the N Reactor in all solutions not containing phosphate. Small cracks were found in the N Reactor tubing exposed in two of the five phosphate-treated waters after 6 to 8 months. No cracks were found in solution-treated or sensitized 304 stainless-steel sheet material, Inconel-600 N Reactor tubing, Incoloy 800, or A-212 carbon steel.

"Straining"-electrode experiments on Fe–Cr–Ni alloys have been conducted at The Ohio State University to test the hypothesis that the tip of an advancing stress-corrosion crack is dynamically strained, thereby producing sufficiently high current densities to propagate the crack by electrochemical dissolution.[8] At strain rates of up to 6%/min, very little change was observed in the current density in the active region during straining. In the lower range of passive potentials, the current density with the straining electrode was not appreciably increased over that with a static electrode. At the critical potential for current increase in the passive region, the current density with the straining electrode was greatly increased over that with a static electrode. The potential was less than the pitting potential. The largest differences between the critical and pitting potentials were observed for $H_2SO_4$ and $H_2SO_4$ + KCl solutions, whereas the smallest differences were observed for $H_2SO_4$ + KBr or KI. The latter two were also less prone to produce stress-corrosion cracking. Nickel in $H_2SO_4$ + KCl solutions showed no significant difference between current density with the straining electrode and that with the static electrode over the whole range of potentials in the passive range.

## Corrosion of Nickel- and Cobalt-Base Alloys

Oxidation studies of Hastelloy X for periods of up to 12,500 hr in air at temperatures from 1300 to 2000°F (705 to 1095°C) have been performed by Aerojet-General.[9] The primary mode of oxidation at 1600°F (870°C) and lower was by thin, intergranular penetration. At 1750°F (955°C) and higher, internal oxidation occurred as a uniform band of small oxide particles distributed intergranularly beneath the metal–oxide interface. The oxidation produced a duplex oxide consisting of a $Cr_2O_3$ inner layer and a $MnCr_2O_4$ spinel outer layer. The oxidation resistance of the Hastelloy X increased as the spinel:$Cr_2O_3$ ratio increased, and the amount of spinel formed increased with increasing manganese content in the alloy.

The oxidation behavior of Hastelloy N is being studied at Oak Ridge.[10d] The addition of silicon to the alloy markedly improved its oxidation resistance, particularly at 982°C, at which temperature the oxidation rate decreased linearly from about 500 mg/(cm$^2$)(1000 hr) at <0.05% silicon to about 15 mg/(cm$^2$)(1000 hr) at 0.6% silicon. At 760°C the oxidation rate at silicon contents >0.05% was <10 mg/(cm$^2$)(1000 hr). Titanium in the range of 0 to 1% had little effect on the oxidation behavior of the Hastelloy N.

The oxidation behavior of nickel- and cobalt-base alloys was determined at Savannah River in connection with encapsulating $^{60}Co$ heat sources.[11] Specimen performance was evaluated on total penetration, which was based on surface-scale thickness (including that which spalled) and depth of intergranular penetration and alloy depletion. After exposure of 9400 to 10,000

hr at 1000°C, TD nickel–Cr was the most resistant material, having a total affected zone of 2.4 mils. Inconel 600, Tophet C, Hastelloy C, GE2541, Haynes 25, and Hastelloy X had affected zones of 8 to 12 mils and were considered acceptable.

The cause of cracking failures of K-Monel bolt studs on autoclaves and pumps has been investigated at Petten, Holland.[12] The cracks were intergranular, and analyses indicated that there was an increase in sulfur and copper content at the grain boundaries. The source of the sulfur was the fatty ingredient in the paste of a high-temperature lubricant that decomposed to liberate sulfides or sulfur at vessel-operating temperatures of 360 to 400°C.

## Corrosion of Other Alloys

Corrosion and wear surveillance in the Plutonium Recycle Test Reactor through December 1967 has been described by Battelle–Northwest.[13] Measurements on coupons exposed in the primary system (water at 265°C and 1070 psi) and in the moderator calandria showed negligible corrosion (<0.004 mil/month) for stainless steel, Zircaloy, and aluminum. Continuous measurements by electrical-resistance probes in the moderator, reflector, top and bottom shield, and core–blanket helium systems indicated negligible corrosion (<0.005 mil/month) for the aluminum and carbon-steel probes. Inspection inside the steam generator revealed that the tube bundle and shell were in good condition. Electrical-resistance probes indicated moderate corrosion rates (0.10 to 0.19 mil/month) in the biological- and thermal-shield systems. Elbows on three steam-generator vent lines were replaced because of failure resulting from localized (trench) corrosion and high stress levels. Two tubes were sealed in the primary-treatment heat exchanger because of leaks that apparently were caused by wear from rubbing against a baffle plate.

Galvanostatic polarization techniques have been used to determine electrochemical corrosion rates of the SNAP-21 radioisotopically fueled power system in seawater at the Naval Radiological Defense Laboratory.[14] A galvanic series was determined, and galvanic currents were measured between coupled materials. On the basis of these results, complete penetration of components would be predicted as follows: aluminum insulation and ring, <1 year; U–8 wt.% Mo alloy biological shield, 3 years (2.5 in.); copper insulation and cold frame, 3 years; stainless-steel liner, ~200 years (0.125 in. thick); and Hastelloy C fuel container, ~600 years (0.25 in. thick).

The crevice corrosion of titanium in 150°C salt solutions has been investigated by Oak Ridge.[15] Results indicated that crevice corrosion under these conditions begins as a result of a differential aeration cell and continues because of an acid concentration developed in the small volume within the crevice. Crevice attack was not specific to chloride solutions but also occurred in iodide, bromide, and sulfate solutions. The more concentrated salts produced the more severe attack. Results of electrochemical polarization studies indicated that alloys which remain passive in nonoxidizing acid salts, such as those containing palladium, molybdenum, or nickel, should be more resistant to crevice attack. (W. E. Berry)

## Corrosion of Refractory Metals

The French[16] have investigated the oxidation of tungsten and rhenium in the temperature range 1127 to 2227°C at oxygen pressures between $5 \times 10^{-6}$ and $3 \times 10^{-4}$ torr. The oxidation rate exhibited a maximum as a function of pressure because of the production of atomic oxygen above 1727°C.

The diffusion of oxygen in niobium oxides has been studied at McMaster University.[17] Single crystals of alpha $Nb_2O_5$ were grown by the Verneuil technique and machined into cylinders; electrical conductivity then was measured as a function of temperature between 600 and 1000°C and oxygen pressure between $10^{-16}$ and 1 atm. By following the resistance change as a function of time on changing the environmental pressure, the diffusion coefficient of oxygen was determined at varying degrees of oxide nonstoichiometry. Diffusion was several hundred times slower in the oxide with the highest degree of nonstoichiometry. A similar study on gamma $Nb_2O_5$ scale stripped from oxidized niobium was conducted, but absolute measurements could not be made because of cracking. Nevertheless, the results indicated similar behavior for both alpha and gamma $Nb_2O_5$.

The Russians[18] have investigated the oxidation of binary Nb–Ta alloys at 550 to 1050°C. For alloys up to 30 at.% tantalum, a decrease in oxidation rate with increasing temperature was noted in the temperature ranges 600 to 700°C and 800 to 1000°C. For alloys containing 30 to 100 at.% tantalum, the decrease was noted only in the lower temperature range. The temperature at which the rate was observed to decrease was related to the oxide-film composition.

Various aspects of tantalum oxidation have been studied. Growth characteristics, morphology, and crystallography of tantalum oxide in the initial stages

of formation after 10 min at 500°C in 1 atm oxygen have been determined.[19,20] The data indicated that formation of $TaO_y$ plates occurred by martensitic transformation. Geometrical effects of oxidation of tantalum tubes at 825 to 930°C in 0.53 atm oxygen have also been described.[21] These results suggest that the major stress generated at the oxidizing surface was in the adherent part of the oxide scale rather than in the surface-metal layers affected by solution of oxygen. A tetragonal phase with $a = 13.32$ and $c = 6.12$ A has been detected in the Ta–O system by electron diffraction.[22]

Adsorption and decomposition of various gases on tungsten have been the subjects of a number of investigations. These studies include the following: (1) adsorption and decomposition of $NH_3$ on (2 1 1) surfaces at 25 to 1000°C using flash desorption and mass spectrometry, low-energy-electron diffraction, and measurements of work-function change,[23] (2) adsorption of CO on (2 1 1) surfaces at 25 to 900°C using LEED,[24] (3) chemisorption of $N_2O$ on tungsten filaments[25] at 25 to 1500°C, and (4) adsorption of oxygen on (1 1 0), (2 1 1), (1 1 1), (1 0 0) surfaces at −195 to 1500°C using field-emission microscopy.[26]

(B. C. Allen)

# Corrosion by Nonaqueous Liquids and Vapors

## Corrosion by Sodium

It has long been recognized that mass transfer in liquid-metal systems can stem from either temperature gradients or concentration gradients. The latter may be significant in high-temperature molten-metal systems where the circulating fluid encounters more than one construction material. A good example would be a sodium-cooled reactor system made of stainless steel, which contains fuel elements clad with a nickel-base alloy or a refractory metal. West German workers studied this dissimilar-metal mass-transfer phenomenon by exposing nickel alloys and molybdenum alloys to flowing sodium in isothermal stainless-steel loops.[27] They found that this caused iron-rich microcrystals ($10^{-3}$ to $10^{-2}$ mm in diameter) to grow at the grain boundaries of the nickel- and molybdenum-alloy specimens. Microprobe studies showed that the crystals had the atom ratios Fe:Mo ≈ 1:1 on molybdenum, Fe:Ni ≈ 2:1 on Incoloy 800, and Fe:Ni = 6:1 to 10:1 on Incoloy 626. Constituents of the stainless steel other than iron were also present in the microcrystals, but in much smaller amounts.

Several studies have given evidence that exposure to hot sodium produces irreversible effects at the grain boundaries of stainless steels. For example, workers at Argonne noted that 304 stainless-steel specimens treated with a modified Strauss reagent underwent much larger increases in electrical resistivity if they had previously been exposed to 1200°F (650°C) sodium than if they had been sensitized in air.[28] To learn more about such grain-boundary effects, Stanford Research workers exposed thin foils of 304 stainless steel to 1200°F sodium for periods up to 110 hr, cleaned the foils thoroughly by repeated washings with solvent in a Soxhlet extractor, and then examined them by transmission electron microscopy.[29] They noted severe grain-boundary attack and the presence of precipitates on the surface, as well as along and within the grain boundaries. The precipitates, which definitely stem from the prior sodium exposure, do not appear to be sodium or sodium oxide. Work is in progress on their identification, and preliminary X-ray indications are that they could be $Cr_{23}C_6$, $Cr_3C_2$, $Cr_2N$, or some combination of these.

At Brookhaven[30] a 1655-hr forced-convection sodium-loop run was completed with specimens of HS-25, UMCO-51, molybdenum, 321 stainless steel, and 304 stainless steel inserted in the all-stainless-steel loop. In the test section the sodium was heated from 710 to 760°C while flowing over the specimens at 22 ft/sec. The oxygen content of the sodium was 4 ± 2 ppm for the first 900 hr, dropping steadily thereafter to ~1 ppm by the end of the test. The molybdenum specimens showed no measurable weight changes. The corrosion rates of the remaining materials decreased with time, leveling off to essentially steady values of <1.5 mils/year by the end of the test.

A second loop was run for 335 hr under the same conditions, except that the oxygen level was maintained below 1 ppm by hot trapping at 650°C and the specimens were made of V–20 Ti, Nb–1 Zr, Mo–0.5 Ti–0.06 Zr (TZM), V–15 Ti–7.5 Cr, V–15 Cr–5 Ti, and 321 stainless steel. The molybdenum alloy showed essentially no weight change, and the Nb–1 Zr gained only 0.1 to 0.2 mg/cm². The vanadium alloys gained on the order of 1 to 2 mg/cm², and the 321 stainless steel lost about the same amount. In each case the weight change increased with increasing temperature in the range 720 to 760°.

Continuing their biaxial-stress-rupture studies on 304 and 316 stainless steels in high-purity sodium (~10 ppm oxygen) and helium (99.99% pure), researchers at Atomics International[31] confirmed the fact that sodium does not degrade the mechanical properties in tests up to 3000 hr at 1200°F (650°C) and 1000 hr at 1400°F (760°C). Further, the use of 10 to 15% cold work reduces the long-term stress-rupture resistance of both steels, enhancing precipitation within grains, weakening the grain boundaries, and promoting sigma-phase and grain-boundary-void formation during stress-rupture testing. At 1000°F (540°C), 10 to 15% cold-worked 304 stainless steel has higher long-term rupture strength than comparable worked 316 stainless steel. At 1200°F the opposite is true. Figure III-1 shows some of the creep-rupture results.

Battelle–Columbus has issued a comprehensive review[32] of the properties and technology of candidate cladding materials for the liquid-metal-cooled fast breeder reactor (LMFBR). Materials covered are selected austenitic stainless steels, nickel-base alloys, and refractory metals. Included in this report is a detailed review of the recent worldwide literature on the compatibility of these materials with sodium.

## Solubility in Sodium

In 1967 Atomics International workers reported that the Arrhenius curve for the solubility of copper in sodium showed a break at 500°C, suggesting a change in the mechanism of solution at this temperature.[28] Subsequent measurements, combined with the results of studies at two other sites, indicated that this is probably not the case. The final composite solubility curve follows the equation[33]

$$\log S \text{ (ppm Cu in Na)} = 5.957 - 3430/T(^\circ\text{K})$$

in the temperature interval 245 to 726°C.

Workers at Argonne[34a] measured the solubility of nitrogen in molten sodium as a possible aid in the understanding and control of nitriding in sodium

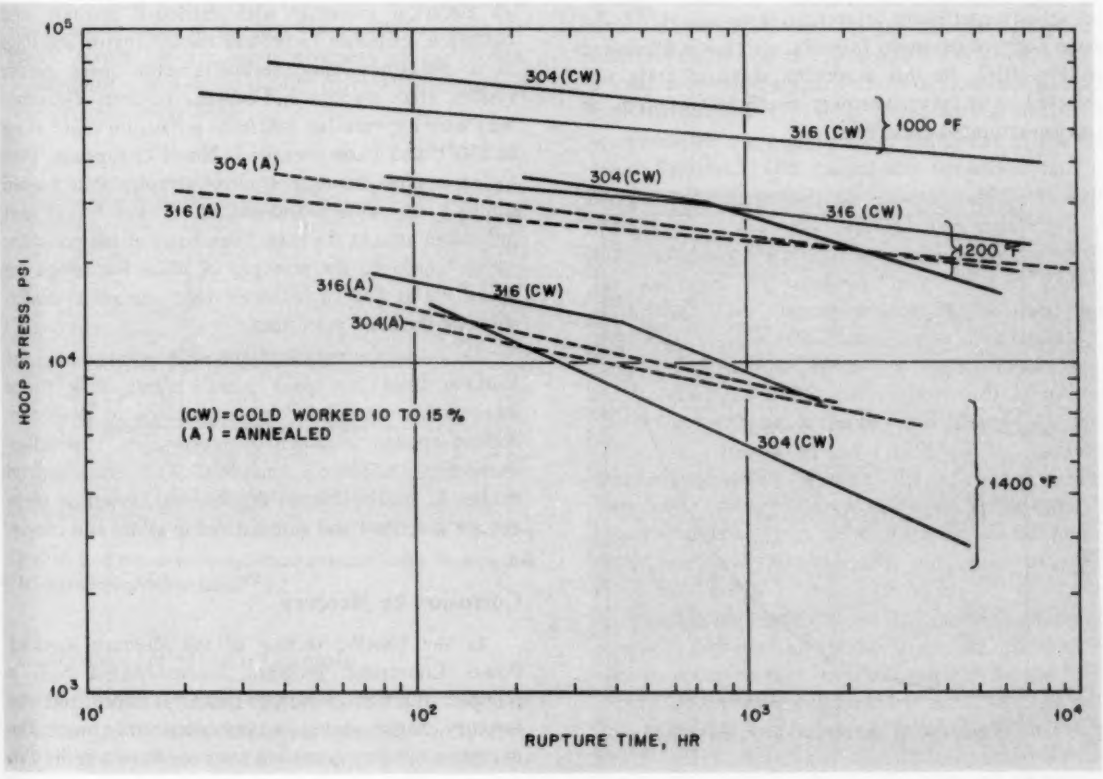



**Fig. III-1 Stress-rupture properties of 304 and 316 stainless steels in 1000, 1200, and 1400°F sodium.[31]**

systems, and also in connection with the possible use of nitrogen-containing blanket gases. The results of at least six measurements at each temperature and 10 atm pressure, using $^{15}N$-tagged nitrogen, are tabulated below.

| Temperature, °C | Solubility/atm pressure, $10^{-12}$ g $N_2$/g Na |
|---|---|
| 451 | 12 ± 8 |
| 502 | 19 ± 7 |
| 550 | 28 ± 8 |
| 600 | 49 ± 9 |

Furthermore, by noting that the stripped-gas samples contained essentially the same distribution of nitrogen isotopes as the gas used to saturate the sodium, it was concluded[35] that nitrogen dissolves diatomically in sodium.

After exposing vanadium wires to sodium at 700°C for 10 hr or more to equilibrate oxygen, Argonne workers were able to use the oxygen-concentration measurements to arrive at a distribution coefficient and an activity coefficient for oxygen in vanadium.[36a] The large negative deviation from Raoult's law is illustrated in Fig. III-2. In this work the standard state was selected as an oxygen-activity coefficient of unity in oxygen-saturated vanadium.

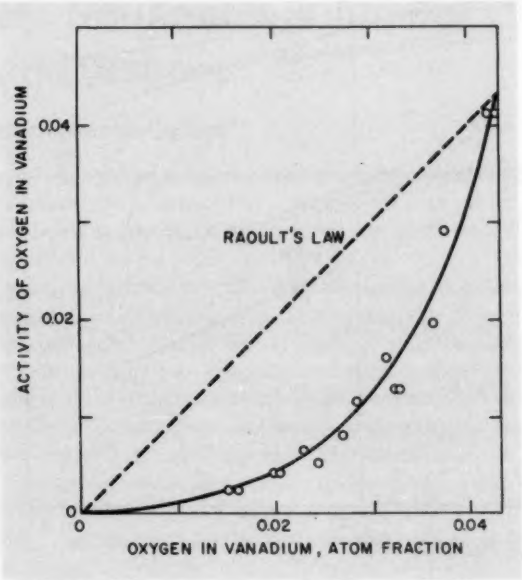



**Fig. III-2 Activity of oxygen in vanadium[36a] at 700°C.**

## Corrosion by Potassium

Six alloys (318 stainless steel, HS-25, Hastelloys C, N, and X, and René 41) were evaluated at NASA's Lewis Research Center[37] for ability to withstand 1800°F (980°C) boiling potassium well enough for use in hardware for ground testing space power-system components. Capsules machined from rod stock of the test alloys were exposed to 1800°F boiling-refluxing potassium and examined metallographically. All of the materials showed some evidence of corrosion. However, only the 318 stainless steel exhibited severe enough attack to be eliminated from further consideration. An interesting sidelight of this work is that the potassium, which contained no more than 20 ppm oxygen initially, showed up to 500 ppm oxygen after the test. The source of the oxygen is unknown, but the greatest pickup occurred in the capsules that were attacked the most. The materials could be arbitrarily ranked into three groups. Most resistant were René 41 and HS-25; next were Hastelloys N, C, and X (in that order); and finally, 318 stainless steel.

Investigators at Eimac conducted studies[38] to find an electrical insulator with sufficient strength and corrosion resistance to protect the alternator windings in a potassium-vapor turboalternator space power system. High alumina and beryllia modulus-of-rupture bars were exposed for 500 hr to potassium vapor at up to 870°C and 2 atm pressure in Nb–1 Zr capsules, then tested in cross bending. Control samples were heated similarly in vacuum and tested. It was found that potassium attacks the grain boundaries of the ceramics, owing largely to the presence of silica. For long-term usefulness at 870°C, ceramics must contain considerably less than 500 ppm silica.

To aid in comparing cesium with potassium as the working fluid for space power plants, Oak Ridge investigators reviewed[39] all experience to date concerning erosion in steam, mercury-vapor, and potassium-vapor turbines. Analytical and experimental studies of turbine-bucket erosion and cavitation damage are described and summarized in tables and curves.

## Corrosion by Mercury

In the SNAP-2 version of the Mercury Rankine Power Conversion Program, reactor-heated NaK is pumped through a NaK-to-mercury boiler and the mercury vapor drives a turbogenerator unit. The extensive mercury-corrosion tests conducted under this program have been summarized in several topical reports by TRW Equipment Laboratories.[40,41] In

addition to over 1 million hr of capsule and loop testing, more than 30,000 hr of boiler-test operation was accumulated. Figure III-3 shows a representative mass-transfer pattern in one of the HS-25 test boiler tubes after 2200 hr of operation. This was the result of selective leaching of various elements from the HS-25. The deposits are predominantly cobalt (95 wt.%), with some iron; the leached zone is depleted in Ni, Cr, and Co, and somewhat enriched in W.

The corrosion products carried by the mercury pose a major system-design problem because of their tendency to deposit in critical areas like mercury-lubricated sleeve-bearing surfaces, lubricant-line filters, the mercury pump, and the turbine nozzles and vanes. These corrosion products have been identified as ferrites, possessing a spinel structure of either the gamma $Me_2C_3$ or $Me_3C_4$ type. Their effects can be minimized by operating the boiler and condenser for at least 200 hr, then flushing with clean mercury and recharging before operating the turboalternater unit. This preconditioning eliminates the bulk of the corrosion products, which drop to a steady-state concentration of around 0.01 ppm in the liquid after reaching a much higher value in the first 100 to 200 hr. Since the major source of corrosion products is the boiler, maintaining a high-vapor quality (over 95%) at the exit will minimize carry-over.

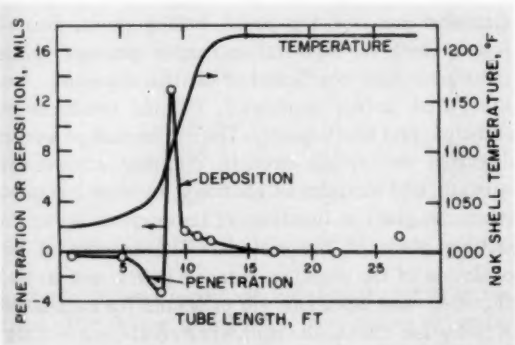



**Fig. III-3 Corrosion–temperature correlation for NaK-heated HS-25 mercury boiler tube.[40]**

## Containers for Molten Uranium

A study at Ames Laboratory[42a] to evaluate yttrium metal as a container material for molten-uranium-alloy fuels has been concluded. Iron additions (0.02 to 10 wt.%) to the U–5 Cr (eutectic) alloy were found to lower the melting point. The predicted solubilities of yttrium in molten uranium, UCr, and UCr–1 Fe at 950°C are 0.042, 0.029, and 0.024 wt.%, respectively, suggesting that the UCr–Fe alloy should be the least corrosive of the three. Actually, capsule tests showed solution attack of yttrium to be slightly greater by UCr–1 Fe than by UCr. With the latter alloy the yttrium-capsule walls suffered about 20 mils of penetration after 3000 hr at 950°C, making this combination appear less promising than it did in preliminary tests.

## Corrosion by Organics

The terphenyl-cooled Piqua Nuclear Power Facility (PNPF) was forced to shut down early in 1966 as a result of fouling of the core by massive carbonaceous deposits. Careful study showed that oxygen exposure and subsequent contamination of the coolant were responsible, although little was known about the rate or the products of terphenyl oxidation—particularly in the presence of radiolysis products. As part of the Heavy-Water Organic-Cooled Reactor (HWOCR) program, workers at Atomics International studied the oxidation of Santowax OM (an orthorich terphenyl mixture) circulating at 350 to 620°F (175 to 325°C) in a small loop while up to 4 vol.% oxygen in argon was bubbled through it.[43] They found that at the higher temperatures the nonterphenyl impurities in the distilled Santowax OM caused the formation rate of oxygenated compounds to increase rapidly at first, then drop off gradually to a high steady-state rate. A film containing about 4 wt.% oxygen was found on the reaction vessel. The radiation dose of $\sim 3 \times 10^6$ rads/hr from the $^{60}Co$ gamma source in the loop was apparently too low to influence the oxidation rate.

Thermal decomposition experiments on irradiated and unirradiated PNPF coolant were also completed. There was no change in composition of samples treated for up to 11 months at 550°F (290°C), but irradiated samples held at 750°F (400°C) for only 6 months were completely converted to high boilers (HB), coke, or gas. The disappearance of terphenyls from the unirradiated Santowax OM at the same temperature occurred much more slowly.

Fretting and wear tests of SAP (sintered aluminum powder) and Zircaloy-2-clad $UO_2$ fuel elements in organic coolants have been summarized by the Canadians.[44] Tests were conducted in Santowax OM with 30% high boilers at temperatures ranging from 316 to 399°C and with thermal cycling from about 340 to 93°C. After 1965 hr of operation and with 30 thermal cycles, an average of 9 rib-to-sheath fret marks were

observed on each SAP-clad element. Maximum penetration was 3.4 mils or 14% of the wall thickness. After 1147 hr of operation and with 13 thermal cycles, an average of 5 wire-wrap-to-sheath fret marks were found on each Zircaloy-2-clad fuel element. Maximum penetration was <1.5 mils or <6% of the wall thickness.

Results of loop experiments in Canada's NRU reactor using Santowax OM and HB-40 (hydrogenated terphenyls) to cool SAP-clad UC fuel bundles[45] showed considerable promise for this system. The fuel operated satisfactorily for 17 months at 20.8 kw/ft peak-power rating and reached a record burnup of 16,700 Mwd/metric ton of uranium. Surface-film formation was effectively inhibited by maintaining a water concentration in the coolant above 50 ppm. Elaborate coolant cleanup was unnecessary. A small bypass flow through an attapulgus-clay column and glass-spool filter was adequate. Even after the cladding defected, it operated satisfactorily for 4½ months without organic logging, fuel–coolant interaction, catastrophic cladding failure, or excessive radiation levels on the main-loop piping. Shutdown and fuel removal were scheduled and routine.

A British patent[46] has been obtained for Euratom on the use of $NH_4OH$ and $CO_2$ additions to an organic coolant or moderator fluid to inhibit corrosion of magnesium or magnesium-alloy fuel claddings.

### Corrosion by Fluoride Salts and Lead

A survey of metal-base structural materials for use in molten lead and fluoride salts at 500 to 1000°C has been published[47] by the Air Force Materials Laboratory. Mechanical properties, fabrication, and corrosion are the major items considered. The study was related to the molten-salt experimental reactor (MOSEL) concept. (E. M. Simons)

## Metal–Water Reactions

The Nuclear Safety Information Center has published a comprehensive review of available data regarding the role of metal–water reactions during a loss-of-coolant accident in a light-water power reactor.[48] The physical chemistry of various metal–water and associated reactions was covered, with emphasis on the reactions of (1) zirconium or Zircaloy with water, (2) stainless steel with water, (3) aluminum with water, (4) $UO_2$ with water, and (5) hydrogen with air. Also, various data were applied to the analysis of reactions occurring during both nuclear-excursion accidents and loss-of-coolant accidents. It was concluded that metal–water reactions would contribute relatively little to the consequences of nuclear-excursion accidents.

In loss-of-coolant accidents, prompt initiation of emergency core-cooling systems would limit the amount of metal–water reaction to a low value. However, possible fragmentation of fuel pins having chemically reacted cladding makes it difficult to ensure meeting of the AEC criterion that the cladding metal–water reaction be limited to negligible amounts. It was concluded that the amount of metal reacted prior to melting of the reactor core would be between 25 and 50% without any emergency core cooling. Hydrogen explosions, often discussed in safety analyses, were not considered credible since hydrogen produced by the metal–water reaction is assumed to be below its flammability limit or is assumed to burn upon release into the containment vessel.

Workers at General Electric have prepared a handbook-type report[49] for use in evaluating light-water-cooled reactor loss-of-coolant accidents involving Zircaloy-4 and 304 stainless-steel-clad $UO_2$. Both boiling-water and pressurized-water reactors are covered. All property values were critically evaluated taking into consideration the meltdown environment of steam or steam and air. The physical properties discussed are: melting point, boiling point, heat of fusion, heat of vaporization, vapor pressure, phase transformations, coefficient of thermal expansion, density, total normal emittance, thermal conductivity, enthalpy, and heat capacity. The mechanical properties discussed are: tensile strength, ductility, compressive strength, and modulus of elasticity. In most instances, values are given as functions of temperature up to the melting point of the material. The kinetics of the oxidation of the cladding materials with steam are also discussed, and equations are presented for calculation of oxidation rates under isothermal conditions in 1 atm steam. For Zircaloy-4 or zirconium with steam, the following equations are recommended.

Between 1000 and 1600°C,

$$\frac{W^2}{t} = 7.10 \times 10^5 \exp(-40{,}500/RT)$$

Between 1600°C and the melting point,

$$\frac{W^2}{t} = 1.5 \times 10^8 \exp\{(-60{,}600 \pm 5400)/RT\}$$

where $W$ = weight gain (oxygen pickup) per unit surface area in mg/cm$^2$
$t$ = time in seconds
$R$ = gas constant in cal/(mole)(°K)
$T$ = absolute temperature

Similarly, for 304 stainless steel in steam above 1000°C

$$\frac{W^2}{t} = 2.4 \times 10^{12} \exp\{(-84{,}000 \pm 2400)/RT\}$$

Additional Transient Reactor Test (TREAT) photographic experiments were performed with Zircaloy-clad fuel rods containing $UO_2$ (5% enriched) pellets.[34b] These specimens were identical in composition and dimensions to the vibrationally compacted $UO_2$ fuel rods tested previously. Comparison of failure of pellets and power (Vibra-Pac) fuel from TREAT photographic tests (see Table III-1) suggested the existence of two modes of fuel failure, for both fuel types. The failure energies for these modes depend in part on the reactor period. The modes were defined as: (1) a *prompt failure*, which occurs during the power transient and is manifested by rapid pressurization within the fuel specimen followed by rupture of the cladding and injection of the fuel into the coolant; (2) a *delayed failure*, which occurs after completion of the transient and is due to the degradation of the cladding by metal–water reaction and fuel–cladding interaction. For reactor periods less than 80 msec, the failure threshold energies by both mechanisms were between 235 and 290 cal/g $UO_2$, independent of fuel type and enrichment. For longer reactor periods the energy required to initiate prompt failure was greater.

(J. M. Genco)

**Table III-1 Summary of TREAT Photographic Tests with Zircaloy-Clad $UO_2$ Fuels[34b]**

| Fuel type | Enrichment, wt.% $^{235}$U | Reactor period, msec | Total transient energy, cal/g $UO_2$ | Energy at failure, cal/g $UO_2$ | Mode of failure |
|---|---|---|---|---|---|
| Vibra-Pac | 5 | 43 | 354 | 235 | Prompt |
| Vibra-Pac | 5 | 48 | 335 | 277 | Prompt |
| Pellet | 5 | 48 | 331 | 291 | Prompt |
| Pellet | 5 | 63 | 263 | 263 | Delayed |
| Pellet | 5 | 66 | 244 | Did not fail | |
| Vibra-Pac | 5 | 67 | 258 | 258 | Delayed |
| Vibra-Pac | 5 | 71 | 233 | Did not fail | |
| Vibra-Pac | 10 | 74 | 357 | 277 | Prompt |
| Vibra-Pac | 5 | 75 | 223 | Did not fail | |
| Pellet | 10 | 80 | 450 | 295 | Prompt |
| Pellet | 10 | 107 | 330 | 330 | Prompt |
| Pellet | 10 | 108 | 290 | 290 | Delayed |

# Radiation Effects in Structural Materials

The proceedings of the Symposium on Radiation Effects, held in September 1965, were published[50] in *Metallurgical Society Conferences*, Vol. 37. The 28 papers presented were concerned mainly with a basic understanding of radiation effects on metals. The 10th Symposium on Special Metallurgy Brittleness and Irradiation Effects held in Saclay, France, is the basis of another publication.[51] The 26 papers presented at this symposium dealt mostly with defects produced by irradiation at low temperatures. Most of the work presented was performed in France.

The results of in-pile creep tests of various materials have been summarized by Battelle–Northwest.[52] It has been found that the creep rate of Zircaloy-2 and Zr–2.5 Nb at 300°C is higher in-pile than out-of-pile. At 350°C the creep rates of these two materials may be higher or lower in-pile, depending on the stress and temperature. Austenitic stainless steels and nickel-base alloys exhibit no radiation-induced changes in creep rates, although the range of second-stage creep is drastically reduced because of decreased ductility. Stress-relaxation tests on zirconium alloys,

stainless steel, and alpha iron during irradiation at 100°C indicate higher creep rates in-pile.

## Zirconium Alloys

Proceedings of the Conference on Use of Zirconium Alloys in Nuclear Reactors at Marianske Lazne, Czechoslovakia, in October 1966, have been published in two volumes.[53] These papers, which are in several languages, contain data on corrosion, mechanical properties, hydride formation, and effects of irradiation on mechanical properties of Zircaloy and other zirconium alloys.

In-pile tensile tests were performed on Zircaloy-4 at 282°C using controlled constant strain rates[54a] from $1 \times 10^{-4}$ to $5 \times 10^{-6}$/hr. The results indicated that the in-pile yield strength of Zircaloy-4, both transverse and longitudinal to the rolling direction, is significantly increased by higher strain rates. However, the out-of-pile yield strength appears to be independent of strain rate for the longitudinal specimens tested.

Enhanced in-reactor relaxation has been observed[55] in Zircaloy-4 and Zr–2.5 Nb–0.5 Cu. This relaxation was found to be temperature dependent with a decrease apparent at lower radiation temperatures. The increased relaxation noted in cold-worked material was especially significant since it was earlier believed that cold work would enhance in-reactor creep resistance. The in-pile relaxation strain in Zircaloy-4 was sensitive to structure, increasing with both increasing amounts of prior plastic deformation and decreasing grain size. The in-pile relaxation behavior appears to be consistent with an accelerated thermal-creep model.

Specimens of Zr–0.5 Nb–1.0 Cr in the annealed, cold-worked, and as-quenched states were irradiated[56] at 50°C to fast fluences up to $1.25 \times 10^{19}$ neutrons/cm$^2$. It was found that the annealed material underwent significant changes in room-temperature tensile properties as shown in Table III-2. However the room-temperature tensile properties of cold-worked (10 and 15%) and as-quenched material were not significantly changed by irradiation to a fast fluence of $1.6 \times 10^{19}$ neutrons/cm$^2$. The effect of postirradiation annealing on the tensile properties is illustrated in Fig. III-4.

**Table III-2 Effect of Irradiation[56] on Tensile Properties of Annealed Zr–0.5 Nb–1 Cr**

| Specimen history | Yield strength (0.2% offset), 1000 psi | Ultimate strength, 1000 psi | Total elongation, % |
|---|---|---|---|
| Cold worked and annealed for 2 hr at 850°C followed by furnace cooling (100°C/hr) | 41.1 | 57.1 | |
| Irradiated to $1.45 \times 10^{18}$ neutrons/cm$^2$ | 42.9 | 60.4 | 22 |
| Irradiated to $6.0 \times 10^{18}$ neutrons/cm$^2$ | 69.3 | 79.5 | 20 |
| Irradiated to $9.5 \times 10^{18}$ neutrons/cm$^2$ | 75.5 | 85.1 | 19 |
| Irradiated to $12.5 \times 10^{18}$ neutrons/cm$^2$ | 79.4 | 86.9 | 16 |

The effect of helium and lithium on the tensile properties of zirconium has been determined.[57] The helium was introduced by irradiating a Zr–B alloy at 100°C until a helium content of ~2 cm$^3$/cm$^3$ of alloy ($1.2 \times 10^{-3}$ atom fraction) was obtained from the $^{10}B(n,\alpha)^7Li$ reaction. In postirradiation tensile tests the yield strength was only slightly affected, whereas the reduction-in-area values were drastically reduced at testing temperatures up to 500°C.

## Stainless Steels and Superalloys

A large volume of research is being conducted on the radiation-induced embrittlement in stainless steels and nickel alloys at elevated temperatures. A thorough treatment concerning the effects of radiation on tensile properties of austenitic stainless steel has been presented by Battelle–Northwest.[58] The variables fluence, neutron spectrum, irradiation temperature, and testing temperature and possible mechanisms which may be responsible for the radiation-induced changes in tensile properties were considered. Specimens of 316 stainless steel were irradiated in the Engineering Test

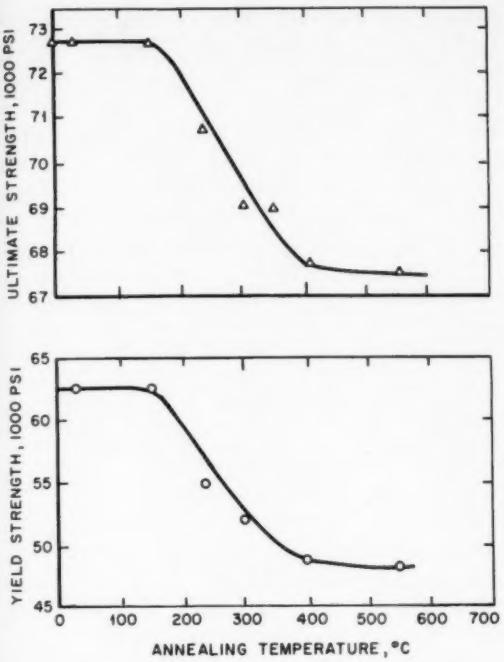



Fig. III-4 Isochronal annealing curves for Zr–0.5 Nb–1 Cr alloy[56] irradiated to $5.5 \times 10^{18}$ neutrons/cm$^2$.

Reactor (ETR) at elevated temperatures (540 to 750°C), whereas 304 and 348 stainless-steel samples were irradiated in the same reactor at low temperatures (290°C); specimens of 304 and 348 stainless steel were also irradiated in the Experimental Breeder Reactor II (EBR-II) at 520°C. It was observed that the radiation-induced increase in yield strength was greater and persisted to higher testing temperatures with increasing fast fluence. As the testing temperature was increased to 750°C, the higher temperature irradiations caused larger increases in yield strength. The results of these tests are given in Fig. III-5. It was suggested that at lower irradiation temperatures a large number of small defects are produced which are subsequently annealed out at the higher testing temperatures. Larger and more stable defects (cavities) are formed during irradiation at higher temperatures. Although these cavities do not cause as large an increase in yield strength as the smaller defects do, they are more stable at higher temperatures, and consequently the radiation-induced yield-strength increase persists to higher test temperatures.

Postirradiation annealing for 1 hr at 1121°C was performed on the specimens that were irradiated in the EBR-II at 520°C to a fluence of $1.1 \times 10^{22}$ neutrons/cm$^2$ (>0.18 Mev). Testing of the annealed specimens at 500°C indicated that both the preirradiation strength and ductility were restored. However, testing at 650°C showed recovery of the preirradiation strength only, whereas the ductility remained the same. Therefore it was concluded that the radiation-induced ductility losses at elevated temperatures are independent of the radiation-induced strength increases due to cavity formation. This conclusion is consistent with the fact that radiation-induced cavities are removed by annealing at 1121°C and the observation that strength increases are dependent on the irradiation temperature (at $10^{21}$ neutrons/cm$^2$) whereas the corresponding ductility decreases are independent of the irradiation temperature.

Studies at Battelle–Columbus[59,60a] have been concerned with the contribution of helium bubbles to grain-boundary weakening and radiation-induced embrittlement in stainless steels at elevated temperatures. Specimens of 347 stainless steel were irradiated to a

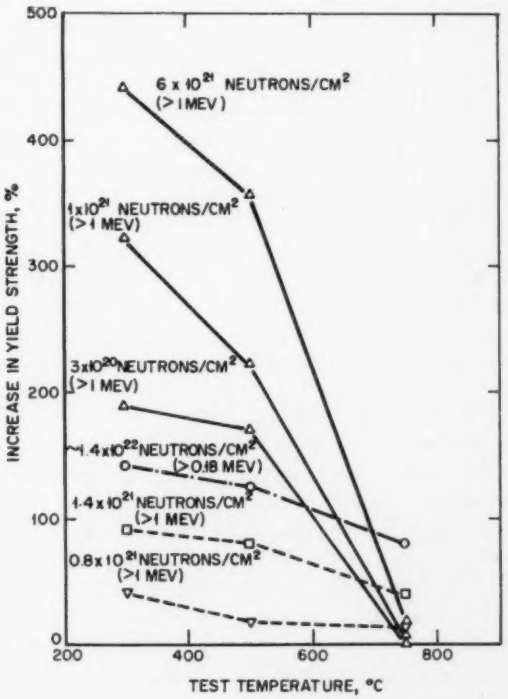

6 x 10^21 NEUTRONS/CM^2 (>1 MEV)
1x10^21 NEUTRONS/CM^2 (>1 MEV)
3x10^20 NEUTRONS/CM^2 (>1 MEV)
1.4x10^22 NEUTRONS/CM^2 (>0.18 MEV)
1.4x10^21 NEUTRONS/CM^2 (>1 MEV)
0.8x10^21 NEUTRONS/CM^2 (>1 MEV)
INCREASE IN YIELD STRENGTH, %
TEST TEMPERATURE, °C

Fig. III-5 Effect of fast fluence and irradiation temperature on the yield strength of austenitic stainless steel.[58] △, ETR 304, 290°C; ○, EBR-II 304, 540°C; □, ETR 316, 600°C; ▽, ETR 316, 700°C.

fast fluence of $2.2 \times 10^{22}$ neutrons/cm$^2$ in the ETR. These specimens contained 0.5 ppm boron, and consequently only 5% of the helium produced originated from the boron impurity. The remaining 95% of the generated helium resulted from $(n,\alpha)$ reactions in the matrix elements iron, chromium, and nickel. Therefore one would expect a uniform distribution of helium and thus little ductility loss in this stainless steel. However, it was found that this stainless steel exhibited greater ductility loss (total elongation being less than 1% at 650°C) than did stainless steels that had an equivalent amount of helium ($\sim 1 \times 10^{-5}$ atom fraction) that originated either from a higher boron impurity or from cyclotron bombardment by alpha particles.

The loss in elevated-temperature ductility in 347 stainless steel irradiated to $2.2 \times 10^{22}$ neutrons/cm$^2$ was also found to be independent of holding times from 4 min to 1 hr before testing at 650°C. These results indicate that the radiation-induced embrittlement at elevated temperature is not diffusion dependent. The extreme degree of radiation-induced loss in uniform elongation (from 18 to 0.7%) could not be explained by weakening of grain boundaries by helium bubbles. Rather, it was suggested that the extreme embrittlement could be caused by either (1) hardening of the grains by small helium bubbles or (2) extension of the ductility minimum as proposed by Rhines.[61] The ductility minimum occurs in many metals and alloys when grain-boundary shear takes place at elevated temperature and causes cracks at the grain boundaries. As the testing temperature is increased, the cracks are healed by grain-boundary migration and the ductility of the material is increased. It was proposed that for the irradiated stainless steel the grain boundaries are pinned by helium bubbles or other transmutation products. Thus the grain-boundary cracks are not healed by grain-boundary migration, and fracture occurs with limited elongation.

French investigators[60b] found that increasing the carbon content from 0.04 to 0.07 wt.% in irradiated 316 stainless steel at 700°C resulted in a decrease in postirradiation elongation from 9 to 2.5% at 700°C. Previous studies indicated that the degree of radiation-induced embrittlement decreased with increasing carbon content.[62] However, it should be noted that the degree of embrittlement is very dependent on the morphology of carbide particles which may result from a given heat-treatment.[64] The tensile specimens used to study the effect of carbon had been irradiated at 700°C to a fast fluence of $1 \times 10^{21}$ neutrons/cm$^2$ and a thermal fluence of $1.7 \times 10^{21}$ neutrons/cm$^2$. No helium bubbles were observed in the as-irradiated stainless steel tested at 700°C. However, annealing the irradiated stainless steel for 1 hr at 1100°C resulted in formation of helium bubbles in the grain boundaries, in twin boundaries, and on dislocations in the matrix. It was also found that the radiation-induced ductility reduction was more severe for specimens irradiated at 650°C than for those irradiated at 800°C, with the fast fluence being $1 \times 10^{21}$ neutrons/cm$^2$ in both cases. The variation of grain size from 31 to 130 $\mu$ did not affect the postirradiation ductility at 700°C. This effect is in contrast to previous observations that the degree of radiation-induced embrittlement at elevated temperatures increased with increasing grain size.[65] Additions of niobium to the 316 stainless steel resulted in a material that was more resistant to radiation-induced embrittlement at elevated temperatures.

Stress-rupture tests were performed at 650 and 700°C for both unirradiated and irradiated ($1 \times 10^{21}$ neutrons/cm$^2$) 316 stainless steel.[60b] The creep rate for the irradiated material was factors of 2 to 10 higher than that for the unirradiated controls. Specimens irradiated at 80°C and annealed for 15 days at 650°C after irradiation exhibited higher creep rates than did specimens irradiated to equivalent fluences at either 550 or 650°C. The results are shown in Fig. III-6.

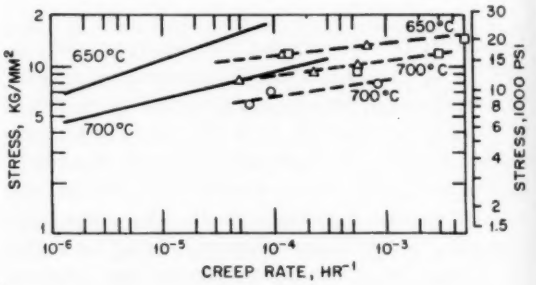



**Fig. III-6 Creep rate of irradiated and unirradiated 316 stainless steel[60b] at 650 and 700°C. ——, thermal control data. - - -, irradiated: ○, $10^{21}$ neutrons/cm$^2$ (>1 Mev) at 80°C + 15 days at 650°C; □, $7 \times 10^{20}$ neutrons/cm$^2$ (>1 Mev) at 550°C; △, $10^{21}$ neutrons/cm$^2$ (>1 Mev) at 650°C.**

Irradiation of stainless steel to a total fluence of $1.6 \times 10^{22}$ neutrons/cm$^2$ in the Dounreay fast reactor was found to result in higher creep rates at 700°C as shown in Fig. III-7. However, in-pile uniaxial creep tests resulted in lower ductilities at fracture, but the creep rate itself did not seem to be affected by irradiation to $8 \times 10^{19}$ neutrons/cm$^2$. The in-pile creep rate of tubular specimens appeared to be

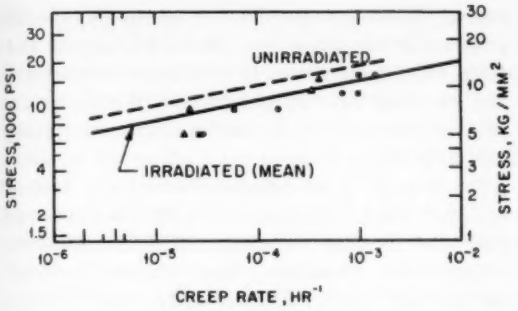



**Fig. III-7 Creep rate of 316 stainless steel irradiated in Dounreay fast reactor to a total fluence of $1.6 \times 10^{22}$ neutrons/cm$^2$ and tested[60b] at 700°C. All specimens annealed 1 hr at 1050°C (= A). △, A + 10% cold work + 100 hr at 800°C; ○, A + 100 hr at 800°C; □, A.**

somewhat higher than the creep rate for uniaxial creep as shown in Fig. III-8.

Stress-rupture tests at 650°C have been conducted on 347 stainless steel irradiated to a fast fluence of $2.2 \times 10^{22}$ neutrons/cm$^2$ in the ETR.[58] Irradiation reduced the rupture life of this material by a factor of about 6. However, the most significant irradiation effect observed was the reduction in elongation at rupture from 20 to about 0.2%. Microstructures of the fractured unirradiated specimen (20% elongation at fracture) showed considerable elongation of the grains and the presence of numerous cracks and voids at the grain boundaries. The fractured irradiated specimen (0.2% elongation at fracture) showed no elongation of the grains and no voids and cracks at the grain boundaries.[66]

Oak Ridge researchers[65] observed that fine-grain stainless steel was less susceptible to radiation-induced

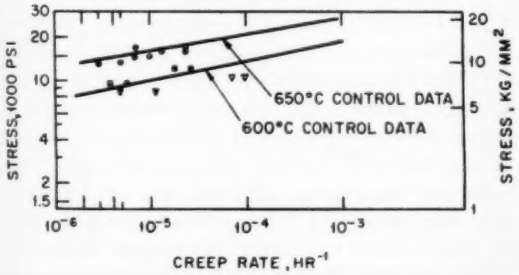



**Fig. III-8 In-pile uniaxial and biaxial creep of 316 stainless steel[60b] at 650 and 700°C. Maximum fluence is $8 \times 10^{19}$ neutrons/cm$^2$ ($E > 1$ Mev). In-pile uniaxial creep tests: ○, 650°C; □, 700°C. In-pile biaxial creep tests: ▽, 650 to 700°C.**

embrittlement at elevated temperatures. To study this effect further, Brookhaven workers[67] obtained a fine structure in 304 stainless-steel specimens by cold working to reduce the cross-sectional area by 92%. There were two intermediate anneals and a final anneal, all at 760°C for 16 hr. These anneals were chosen to obtain a fully recrystallized structure that would be stable at 650°C. The recrystallized specimens were irradiated at a temperature below 100°C to a fast fluence of $1.3 \times 10^{20}$ neutrons/cm$^2$ ($E > 0.82$ Mev). Results of tensile tests on the irradiated and control specimens (Table III-3) indicate that irradiation does not significantly affect the strength at the different testing temperatures; although the ductility is approximately halved by irradiation, it is substantially greater than that of commercial 304 stainless steel under the same conditions.

The radiation-induced embrittlement in stainless steel at elevated temperatures was duplicated when specimens of 316 stainless steel were cold worked,

**Table III-3 Tensile Properties of Heavily Cold-Worked* 304 Stainless Steel[67]**

| Test temp., °C | Yield strength, psi | Tensile strength, psi | Total elongation, % |
|---|---|---|---|
| | **Unirradiated†** | | |
| 25 | 55,000 | 115,000 | 47 |
| 650 | 23,300 | 31,500 | 76 |
| 750 | 10,200 | 13,000 | 53 |
| 800 | 6,600 | 8,650 | 83 |
| | **Irradiated to $1.3 \times 10^{20}$ neutrons/cm$^2$ ($E > 0.82$ Mev)†** | | |
| 650 | 22,150 | 30,600 | 36 |
| 650 | 22,800 | 29,500 | 34 |
| 750 | 12,500 | 13,300 | 29.5 |
| 750 | 11,100 | 12,600 | 24 |
| 800 | 5,500 | 8,300 | 46.5 |

*Cold swaged 92% with two intermediate anneals and the final anneal at 760°C for 16 hr.

†All specimens were tested at a strain rate of 0.2%/min.

annealed, and bombarded with alpha particles in a cyclotron.[68] A total of $4 \times 10^{-5}$ atom fraction of helium was introduced into the steel while its temperature was kept below 150°C. One of the microstructures exhibited $M_{23}C_6$ precipitates at the grain boundaries, whereas the other microstructure con-

tained both carbides and sigma phase. The presence of helium was found to have no effect on the yield or ultimate strength at the testing temperatures of 540 to 815°C. However, the total elongation was significantly reduced by the helium as illustrated in Fig. III-9. It was believed that helium formed bubbles on the grain-boundary carbide particles, thus reducing the ductility and greatly reducing the amount of grain-boundary sliding needed to form a void. A fine dispersion of sigma phase apparently trapped the helium bubbles, thus raising the temperature at which the ductility loss starts to take place.

For further study of void formation in 304 stainless steel, samples from an EBR-II control-rod shroud have been subjected to density measurement by immersion, and selected thin films have been prepared for transmission electron microscopy.[34c,36b] A comparison of the measured density changes with those predicted by transmission electron microscopy (TEM) for the different irradiation conditions showed the density decreases predicted by TEM to be consistently lower than those determined by density measurements. It appears that some of the smaller voids are not being resolved by TEM.

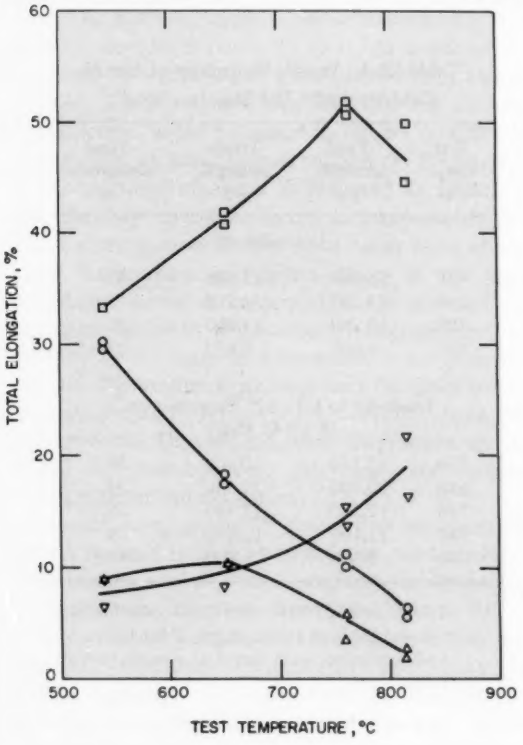



**Fig. III-9 Total elongation as a function of test temperature for 316 stainless steel with no helium and with $4 \times 10^{-5}$ atom fraction helium.[68] Carbides at grain boundaries: □, no helium; ○, $4 \times 10^{-5}$ atom fraction helium. Sigma dispersed in matrix: ▽, no helium; △, $4 \times 10^{-5}$ atom fraction helium. Strain rate = 0.02 $min^{-1}$.**

The French[54b] have studied the effect of irradiation to $1 \times 10^{20}$ neutrons/$cm^2$ on the elevated-temperature ductility of various materials with face-centered cubic structures. The materials included stainless steel (17 Cr–13 Ni–0.2 Ti), pure Ni, Cu, Cu–Si alloy, and Nimonic 80A. Postirradiation ductility of the stainless steel was found to be quite dependent on the carbon content, which is in agreement with the work by French investigators that was discussed earlier.[60b] The maximum postirradiation ductility was obtained for a carbon content of 0.016%, which was believed to result in ideal precipitation of carbides. The postirradiation behavior of copper at elevated temperatures was comparable to that of unirradiated copper containing silicon additions. It is postulated that the intermetallic Cu–Si particles prevent grain-boundary migration during testing and thus cause intergranular fracture with minimal strain. In irradiated copper the grain-boundary pinning is attributed to cavities that are formed during tensile testing. It was concluded from these studies that radiation-induced embrittlement at elevated temperature occurs in materials which are susceptible to intergranular fracture in the unirradiated form. The controlling mechanism was believed to be pinning of grain boundaries by cavities that are produced, or at least stabilized, by helium.

The postirradiation tensile behavior of various Fe–Cr steels at elevated temperatures was investigated by the Germans.[60c] It had been previously found that the onset of embrittlement corresponded with the $\alpha \rightarrow \gamma$ transformation. With chromium contents of 11.3, 14.6, and 17.7 wt.%, it was possible to obtain $\alpha \rightarrow \gamma$ transformation temperatures at 800, 850, and 900°C for the different alloys. These temperatures are only approximate since the transformation is fairly sluggish. After the alloys were irradiated at 50°C to a thermal fluence of $5 \times 10^{19}$ neutrons/$cm^2$ and tested at elevated temperature, embrittlement was found to occur only after the $\alpha \rightarrow \gamma$ transition had taken place. The boron content of these alloys varied from 1 to 70 ppm; however, helium generation was not a significant factor since all of the alloys were embrittled to about the same degree. Specimens of body-centered cubic 15Mo3 steel (0.13 wt.% carbon and 0.24 wt.% molybdenum) were also irradiated for comparison

since this ferritic alloy exhibits intergranular fracture when the unirradiated alloy is tested at elevated temperatures. Tensile tests on unirradiated and irradiated ($5 \times 10^{19}$ neutrons/cm$^2$) specimens showed that the ferritic alloy was significantly embrittled by irradiation before the $\alpha \rightarrow \gamma$ transformation took place. Therefore it was concluded that the elevated-temperature embrittlement occurred in materials that were susceptible to intergranular fracture.

The effects of titanium and carbon contents and grain size on the creep properties of irradiated Incoloy 800 have been studied at Oak Ridge.[69] Specimens of Incoloy 800 were irradiated at 650 and 700°C to a fast fluence of $8 \times 10^{20}$ neutrons/cm$^2$. Figure III-10 shows the effects of grain size and carbon content on creep elongation of irradiated Incoloy 800 at 700°C. It appears that postirradiation creep elongation of the alloy with high carbon (0.12 wt.%) is more sensitive to grain size, with the smaller grain size favoring higher postirradiation creep elongations. Highest creep elongations are obtained with a titanium content of 0.1 wt.% regardless of the carbon content. Figure III-11 shows that the highest rupture lives at a stress of 12,000 psi were obtained with the larger grain size, whereas the carbon and titanium contents appear to be secondary factors.

The effect of irradiation on the superplasticity of an Fe–28 Cr–32 Ni alloy at elevated temperatures has been established at Brookhaven.[67] Unirradiated and postirradiation tensile properties of the superplastic alloy were determined at 650 to 800°C. The elongation at 750°C was reduced from 175 to 17% by a fast fluence of $1.3 \times 10^{20}$ neutrons/cm$^2$. Annealing of the irradiated superplastic alloy for 2 hr at 1000°C resulted in further reduction of the postirradiation ductility from 17 to 9%.

The effects of irradiation at 370°C to a fast fluence of $1 \times 10^{19}$ neutrons/cm$^2$ in the EBR-II on the impact properties of Inconel X750 and 17-4PH stainless steel were determined at Argonne.[36b] The specimens irradiated in helium and sodium seemed to behave similarly, and consequently it was concluded that irradiation in a sodium environment has no discernible effect on impact strength. Reductions in

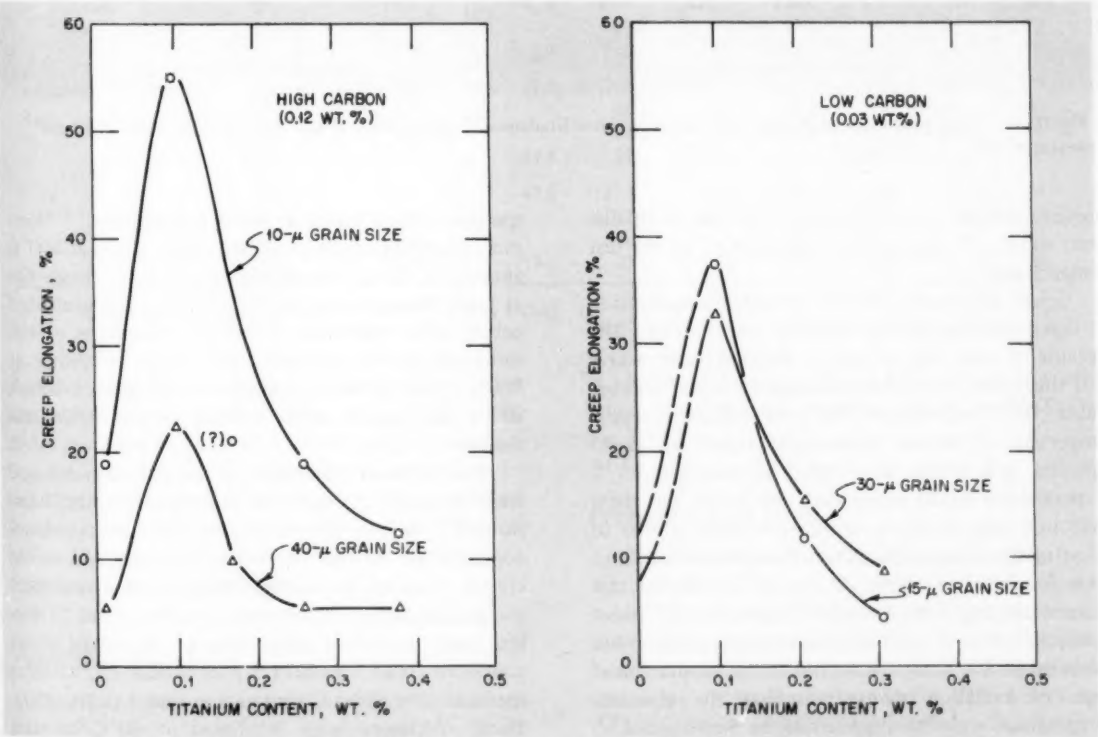



Fig. III-10 Creep elongation of Incoloy 800 at 700°C after irradiation[69] in the ORR at 650 and 700°C to about $0.8 \times 10^{21}$ neutrons/cm$^2$.

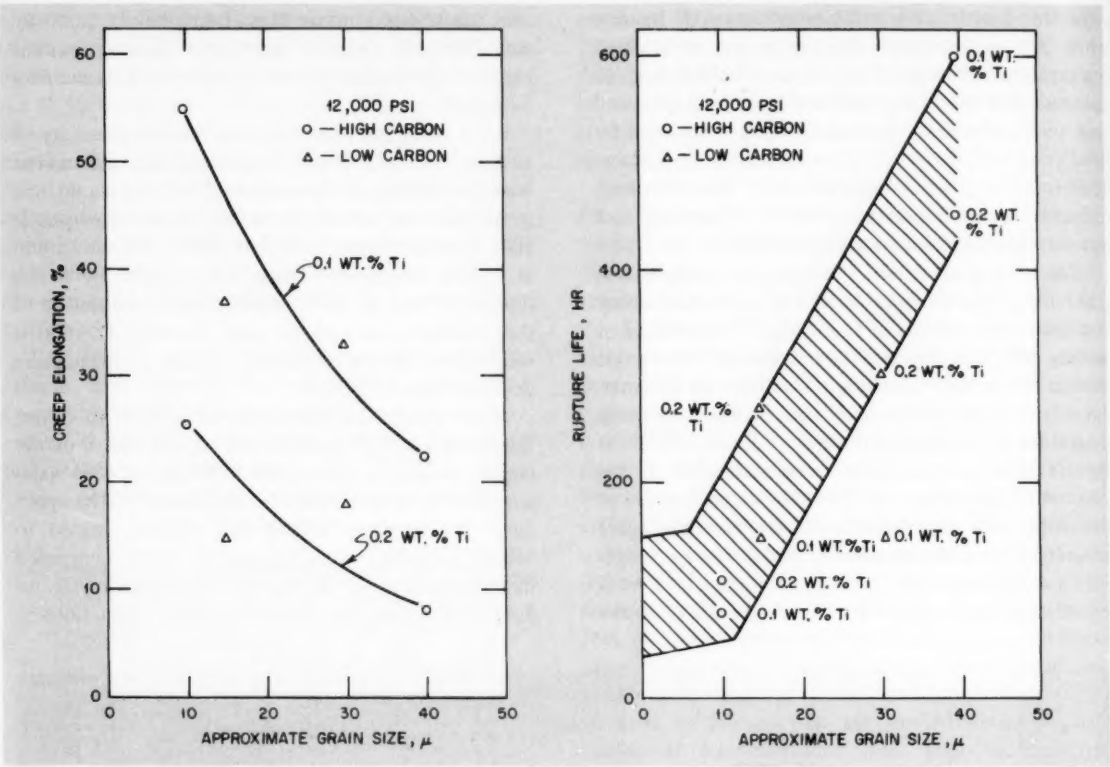



**Fig. III-11 Creep properties of Incoloy 800 at 700°C after irradiation[69] in the ORR at 650 and 760°C to about 0.8 x $10^{21}$ neutrons/$cm^2$.**

impact strengths of X750 and 17-4PH due to irradiation were 1.5 and 2 ft-lb, respectively, at all test temperatures.

Cobalt alloys are attractive for possible application in liquid-metal-cooled fast breeder reactors (LMFBR) because of their high strength at elevated temperatures and their good corrosion resistance to liquid sodium. Table III-4 summarizes the postirradiation tensile properties of various commercial cobalt alloys irradiated and tested at elevated temperatures.[66,70] Experimental cobalt alloys were also tested, but these exhibited postirradiation tensile properties similar to those of the commercial alloys. The commercial alloys were irradiated at about 50 to 100°C with the fast fluence ranging from 1.3 x $10^{20}$ to 1.4 x $10^{20}$ neutrons/$cm^2$. In one study the irradiated specimens were annealed at 800°C for 1 hr to remove the displacement type of radiation damage so that the elevated-temperature embrittlement could be investigated.[71] Table III-4 shows that irradiation resulted in increases in strength and reductions in ductility when the specimens were tested at room temperature.[70] However, annealing of the irradiated cobalt alloys at 800°C appears to restore the preirradiation tensile properties at room temperature and 315°C. All of the irradiated cobalt alloys exhibited significant reductions in elevated-temperature ductility, even after annealing at 800°C. The elevated-temperature strength of cobalt alloys also appears to be reduced by the higher fast fluences.

The influence of nickel on the radiation-induced embrittlement at elevated temperatures has been studied[66] with a series of alloys of varying nickel content. All of the alloys had face-centered cubic crystal structures and included Nickel 200, a nonnickel manganese-stabilized austenitic stainless steel (Tenelon), and two cobalt alloys. One of the cobalt alloys contained 10 wt.% nickel (Haynes Stellite 25) whereas the other one did not contain any nickel (UMCo-50). These specimens were irradiated at 50°C to fast fluences ranging from 1.4 x $10^{21}$ to 1.5 x $10^{21}$ neutrons/$cm^2$. All of the alloys underwent reductions in

**Table III-4 Tensile Properties of Irradiated and Unirradiated Cobalt-Base Alloys**

| Alloy | Test temp., °C | Fast fluence, $10^{20}$ neutrons/cm$^2$ | Yield strength, 1000 psi | | Ultimate tensile strength, 1000 psi | | Total elongation, % | | Ref. |
|---|---|---|---|---|---|---|---|---|---|
| | | | Unirr. | Irr. | Unirr. | Irr. | Unirr. | Irr. | |
| Haynes Stellite 25 | RT | 1.3 | 67.0 | 139.0 | 152.0 | 142 | 55.0 | 15.0 | 70 |
| | 650 | 1.3 | | 45.6 | | 70.6 | | 17 | 70 |
| | 750 | 1.3 | | 35.0 | | 38.2 | | 9.2 | 70 |
| | 800 | 1.3 | 35.9 | 39.2 | 41.5 | 41.5 | 10.5 | 2.3 | 70 |
| | RT* | 14 | 66.3 | 56.2 | 139 | 133 | 68 | 55.6 | 66 |
| | 315* | 14 | 39.7 | 36.0 | 118.5 | 117 | 86 | 60.2 | 66 |
| | 450* | 14 | 36.1 | 29.9 | 96.3 | 70.3 | 42 | 22.8 | 66 |
| | 500* | 14 | | 31.0 | | 66.5 | | 17.0 | 66 |
| | 550* | 14 | 33.9 | 28.5 | 82.3 | 53.5 | 30 | 8.8 | 66 |
| | 650* | 14 | 32.3 | 29.8 | 69.3 | 40.5 | 17 | 4.5 | 66 |
| UMCo-50 | RT* | 14 | 47.5 | | 126 | 127 | 35 | 27.4 | 66 |
| | 315* | 14 | 33.6 | 29.7 | 121 | 112.1 | 61 | 56.7 | 66 |
| | 450* | 14 | 28.9 | 26.0 | 82.5 | 75.1 | 24.5 | 30.7 | 66 |
| | 550* | 14 | 25.0 | 24.6 | 72.0 | 49.1 | 27 | 13.9 | 66 |
| UMCo-51 | 25 | 1.3 | 84.7 | 120 | 171 | 146 | 36 | 20 | 70 |
| | 650 | 1.3 | 37.8 | 46.4 | 72.2 | 68.6 | 14 | 9 | 70 |
| | 750 | 1.3 | | 38.7 | | 46.6 | | 7.5 | 70 |
| | 800 | 1.3 | 30.0 | 34.2 | 40.3 | 39.8 | 10 | 6.5 | 70 |
| Multimet | 25 | 1.3 | 71.0 | 116 | 121 | 138.0 | 43 | 31 | 70 |
| | 650 | 1.3 | | 28.1 | | 53.5 | | 11 | 70 |
| | 800 | 1.3 | 23.6 | 30.0 | 32.9 | 31.3 | 55 | 6.7 | 70 |
| Haynes 188 | 25 | 1.3 | 71.6 | 133 | 142.5 | 167 | 25 | 44 | 70 |
| | 650 | 1.3 | | 46.1 | | 60.8 | | 10 | 70 |
| | 750 | 1.3 | | 38.6 | | 38.6 | | 3 | 70 |
| | 800 | 1.3 | 37.5 | 37.4 | 45.5 | 37.4 | 65 | 1.5 | 70 |
| S-1 | 25 | 1.3 | 47.0 | 114 | 95.2 | 118 | 18.5 | 4 | 70 |
| | 650 | 1.3 | | 37.9 | | 47.4 | | 5 | 70 |
| | 750 | 1.3 | | 30.5 | | 31.7 | | 2 | 70 |
| | 800 | 1.3 | 19.5 | 23.6 | 33.8 | 23.6 | 29.0 | 1.5 | 70 |

*Specimens were annealed for 1 hr at 800°C before testing.

ductility and strength at elevated temperatures after irradiation. Results of the tensile tests on the cobalt alloys are given in Table III-4. Metallographic examination of the fractured specimens indicated that irradiation promoted intergranular fracture at elevated temperatures in all four alloys. The fracture mode of Nickel 200 at 500°C was changed from transgranular to intergranular by irradiation.

## Vanadium Alloys

The creep properties of irradiated V–20 Ti alloys at 650°C were determined at Argonne.[34c] These specimens were irradiated in the EBR-II at 585°C to total fluences ranging up to 2.1 x $10^{22}$ neutrons/cm$^2$. Irradiation apparently has no influence on the minimum creep rate of vanadium alloys at 650°C (see Fig. III-12).

## Pressure-Vessel Steels

The Naval Research Laboratory has investigated[71] the contribution of minor composition differences in A-302B to the radiation-induced shift in the ductile-to-brittle transition temperature. A vacuum-melted heat that was low in residual elements was found to be insensitive to irradiation at 550°F (290°C). It was established that copper and phosphorus contribute to the radiation-induced nil ductility temperature (NDT) increase whereas nitrogen and sulfur do not. Vanadium

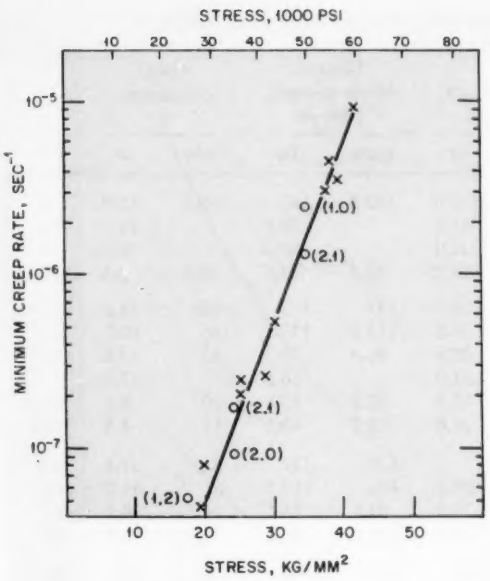



**Fig. III-12 Minimum creep rate of unirradiated and irradiated V–20 Ti alloy[34c] at 650°C. ×, unirradiated; ○, irradiated. Numbers in parentheses indicate the fluence in $10^{22}$ neutrons/cm$^2$.**

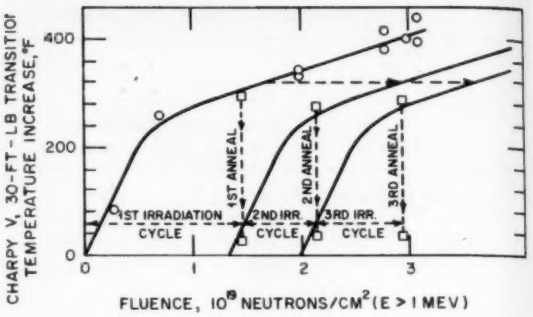



**Fig. III-13 Response of the SM-1A pressure-vessel steel to cyclic irradiation and annealing.[72] Annealed at 585°F for 168 hr; irradiation temperature < 240°F. ○, NDT shift vs. exposure for SM-1A steel (damage path); □, end points of irradiation and annealing cycles.**

was found to increase the embrittlement sensitivity of steel. Long-term aging (1440 hr) at 550°F had only a minor influence on the NDT shift of the steels with the various impurity contents. Consequently, it was concluded that the measured NDT shifts after irradiation were independent of the thermal treatments but were dependent on the differences in composition.

If the radiation-induced shift in NDT becomes significant and perils the operation of a pressure vessel, it may be possible to alleviate this problem by in-place annealing.[72] Figure III-13 illustrates the response of the A-350-LF-1 steel to cyclic irradiation at 430°F (220°C) followed by annealing at 585°F (305°C) for 168 hr. The SM-1A reactor pressure vessel was actually annealed at 585°F to restore its NDT, which was approaching the NDT + 60°F criterion. It is suggested that NDT increases can be minimized by using more shielding, selecting insensitive steels, and utilizing in-place annealing.

Workers at Southwest Research Institute have completed the surveillance of the Elk River reactor pressure vessel.[73] The surveillance specimens received a maximum fast fluence of $1.7 \times 10^{19}$ neutrons/cm$^2$ at an irradiation temperature of 550°F (290°C). The maximum shift in the ductile-to-brittle transition temperature was found to be 130°F (55°C); this occurred in A-302B material originally in the strained and stress-relieved condition. The room-temperature low-cycle fatigue strengths of smooth tensile specimens of pressure-vessel and dissimilar weld-joint materials were increased by the fast-neutron exposure. The fatigue strength appears to increase with increasing fluence as shown in Fig. III-14.

Japanese investigators[74] have compared the response of weld metal, the heat-affected zone (HAZ), and the base metal of modified HY 80 steel to irradiation at 165°F (75°C) to a fast fluence of $3.2 \times 10^{19}$ neutrons/cm$^2$. Tests on Charpy V-notch impact specimens indicated transition-temperature

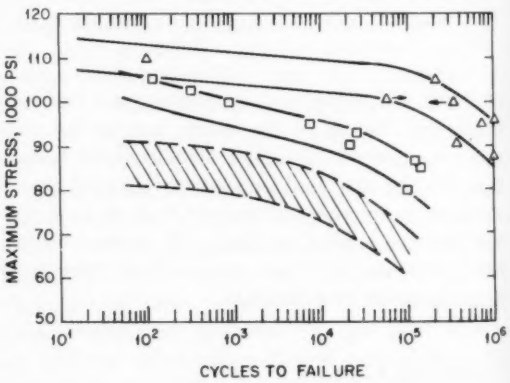



**Fig. III-14 Effect of neutron irradiation[73] on fatigue properties of A-302B. ▨, unirradiated; □, irradiated to $8.3 \times 10^{19}$ neutrons/cm$^2$ (>1 Mev); △, irradiated to $1.48 \times 10^{19}$ neutrons/cm$^2$ (>1 Mev).**

shifts of 330°F (165°C) for the weld metal and 300°F (149°C) for the heat-affected zone. These changes in transition temperature were about equivalent to the change in the base metal.

## Basic Studies of Radiation Effects

Chromium prepared by double melting in an inert atmosphere and irradiated at 80°C to a fast fluence of $10^{20}$ neutrons/cm$^2$ was annealed at temperatures up to 900°C to investigate thermal hardening effects.[75] The results of postirradiation annealing for 1 hr at the various temperatures indicated that a significant thermal hardening occurred in the temperature range 300 to 600°C. An annealing temperature of 900°C was required for the irradiated chromium to obtain a hardness similar to that of the unirradiated control. It was also found that irradiated chromium did not experience additional hardness increases until a total deformation of 80% was achieved. The hardness of the unirradiated control specimen increased progressively with increased deformation. Above 80% deformation the hardness of the control and irradiated specimens increased at the same rate with increasing cold work.

Chromium containing total impurities of 0.025 wt.% (mostly oxygen and nitrogen) was irradiated[76] to a fast fluence of $2 \times 10^{19}$ neutrons/cm$^2$ at 85°C. Examination of thin films of irradiated chromium by electron microscopy revealed dark spots, which were identified as defect clusters. These defect clusters changed to loops when the irradiated material was annealed between 600 and 800°C. It was further noted that irradiation decreased the brittle-to-ductile transition temperature 200°C. Unirradiated chromium exhibits brittle fracture in tension tests at test temperatures up to 200°C; however, the fracture mode of irradiated chromium changed from brittle to ductile above 25°C and exhibited a strain of 60% at 50°C. The improved ductility was attributed to the fact that the critical stage in fracture was changed from crack nucleation in the unirradiated material to crack propagation in the irradiated material.

The radiation-induced increase in the yield strength of most metals has been shown to depend generally on the square root of fluence. Figure III-15 illustrates that the relation exists for irradiated niobium at lower fluences ($<10^{18}$ neutrons/cm$^2$), but a different behavior is evident at higher fluences.[69] The saturation in radiation-induced strength increase may be due to overlap of defect clusters, lack of nucleation of clusters after a certain fluence, or exhaustion of interstitial impurities that stabilize defect clusters. Annealing of

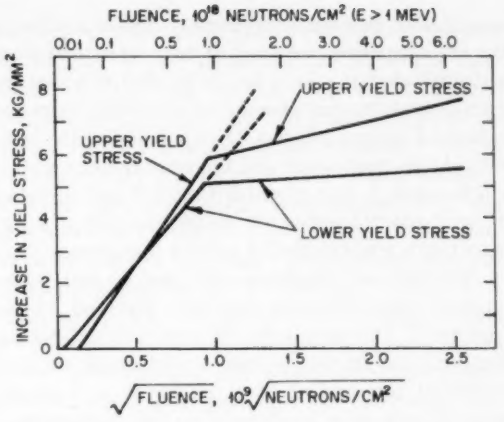

FLUENCE, 10^18 NEUTRONS/CM^2 (E > 1 MEV)
0.01 0.1 0.5 1.0 2.0 3.0 4.0 5.0 6.0
INCREASE IN YIELD STRESS, KG/MM^2
UPPER YIELD STRESS
UPPER YIELD STRESS
LOWER YIELD STRESS
0 0.5 1.0 1.5 2.0 2.5
√FLUENCE, 10^9 √NEUTRONS/CM^2

**Fig. III-15 Effect of irradiation on yield stress of polycrystalline niobium.[69] (Irradiation temperature, <50°C; test temperature, 25°C.)**

the irradiated ($2 \times 10^{18}$ neutrons/cm$^2$) specimens at different temperatures before testing resulted in a variable strength increase as illustrated in Fig. III-16. The fact that the increase in yield strength occurs in the 200 to 400°C range suggests that it is due to the migration of mobile carbon atoms to defect clusters. Electron-transmission-microscopy observations showed that, with increasing annealing temperature, large defects are formed by condensation of interstitial atoms. The areas near the grain boundaries appear to be denuded of the large defects.

Microstructural damage and subsequent recovery in molybdenum irradiated at 600°C was studied by

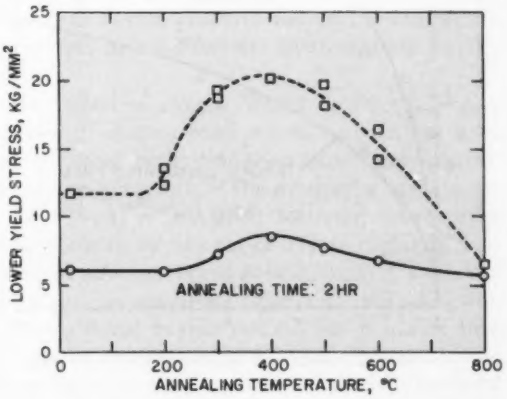



**Fig. III-16 Effect of annealing on the lower yield strength of irradiated niobium.[69] □, fluence = $2 \times 10^{18}$ neutrons/cm$^2$ ($E > 1$ Mev); ○, unirradiated.**

quantitative electron microscopy.[77] After irradiation the microstructure consisted of large interstitial loops and small clusters within the grains. The area near the grain boundaries was denuded of interstitial loops but contained vacancy clusters. During annealing the interstitial loops disappeared and the vacancy loops grew at a rate equal to that of self-diffusion. Rapid annealing of small clusters within the grains occurred at a rate more nearly equal to that of vacancy migration.

Recovery of irradiated and cold-worked body-centered cubic materials has been reviewed by the Belgians.[78] The metals Fe, W, Mo, Ta, and Nb are discussed, and special emphasis is given to the effect of interstitial elements on stage III recovery. Tungsten single crystals were irradiated[79] to fast fluences ranging from $1 \times 10^{18}$ to $2.5 \times 10^{19}$ neutrons/cm$^2$. It was found that the temperature for stage III recovery (~350°C) shifts about 100°C when the fluence level is increased from $1 \times 10^{18}$ to $2.5 \times 10^{19}$ neutrons/cm$^2$.

It is believed that the saturation of radiation-induced yield-strength increase is dependent on the amount of carbon in solution, which governs the capture diameter. Good agreement was found[80] between the predicted and measured increases in yield stress for irradiated Ferrovac Fe and Fe–0.1 C as shown in Fig. III-17. Table III-5 summarizes the expected capture diameter and the predicted fast fluence

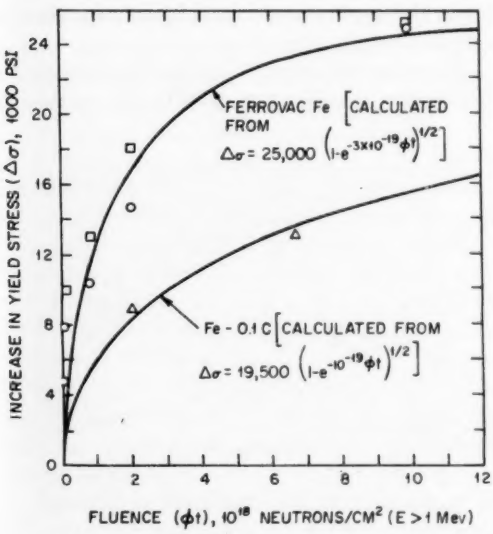



**Fig. III-17 Comparison of predicted and measured irradiation-induced yield-strength changes in iron[80] irradiated at 50 to 100°C. □, △: $\Delta\sigma$ measured at room temperature; ○: $-\Delta\sigma$ measured at 145°K.**

**Table III-5 Estimated Saturation Fluences for Iron and Steels[80]**

| Material | Capture diameter, A | Actual diameter (est.), A | Saturation fluence, neutrons/cm$^2$ ($E$ > 1 Mev) |
|---|---|---|---|
| Ferrovac Fe | 94 | 50 | $1.3 \times 10^{19}$ |
| Fe–0.1 C | 66 | 33 | $4 \times 10^{19}$ |
| A-212B | 61 | 30 | $5 \times 10^{19}$ |
| HY80 | 41 | 20 | $1.6 \times 10^{19}$ |

when saturation takes place in pure iron and in different steels.

Internal-friction experiments were performed on copper of two purities (O.F.H.C. copper of 99.95% nominal purity and 99.999% pure copper)[81] after irradiation to $2 \times 10^{11}$ neutrons/cm$^2$. It was concluded that the defect responsible for the pinning effect observed at slightly above room temperature in neutron-irradiated copper is not due to a simple vacancy mechanism but, rather, is probably due to the delayed arrival of impurity-trapped vacancies at the dislocations. The activation energy of 1.03 ± 0.07 ev, which has been found to govern the pinning centered around 70°C, is in agreement with the results of other workers, but it is considered too high to be associated with the migration of free vacancies. It is also inferred that the release of vacancies from impurity traps is involved. A further pinning stage has been observed, centered around 150°C. It is believed that this pinning stage is due either to the release of further impurity-trapped vacancies or to the annealing of more complex damage such as dislocation loops.

The effect of irradiation on the martensitic transformation in metastable beta brass has been studied at the University of Florida.[82] The brass was irradiated to fast fluences ranging from $5 \times 10^{16}$ to $5 \times 10^{18}$ neutrons/cm$^2$. Neutron irradiation decreased the martensitic-start temperature ($M_s$) about 8°C and increased the maximum rate of transformation; $M_s$ was further decreased when the irradiated brass was annealed at 150°C. (M. Kangilaski)

# Metallurgy of Refractory Metals

The British[83] have studied the deformation of single crystals of Nb–Mo alloys as a function of

composition, orientation, and temperature. Strong solid-solution hardening was observed which reached a maximum at the equiatomic composition. This hardening was attributed to the difference in atomic size between the two elements. Conjugate slip was extensive in the dilute alloy samples. At the 50 at.% composition, deformation occurred mainly by primary slip, and the onset of conjugate slip gave rise to failure by cleavage on (1 0 0). The variation of yield stress of the Nb–50 at.% Mo alloy with orientation was consistent with slip on (0 1 1)(1 1 1) slip systems. The temperature dependence of the yield stress at –196 and 250°C was similar to that of pure body-centered cubic metals, but at a much higher stress level. No evidence of twinning was found.

At NASA–Lewis, yielding, work hardening, and cleavage in Ta–Re alloy single crystals was investigated.[84] The crystals were evaluated in tension and compression as a function of solute concentration and temperature. The temperature dependence of the yield stress in tantalum was decreased by alloying with a minimum being observed at about 2 at.% rhenium. Three-stage hardening was not observed in these alloys. The alloys became more prone to cleavage with increasing rhenium content because of an increasing yield strength rather than a change in cleavage strength. Comparisons were made with other body-centered cubic alloy systems by quantitative calculations to show that the predominant hardening mechanism is due to the interaction of dislocations with misfitting solute atoms close to their slip planes.

The effects of metallic carbides and borides on the strength of Nb–W alloys and of ternary alloys with tantalum at temperatures close to 0.5 $T_m$ have been determined by the British.[85] The alloys were room-temperature forged, solution treated, and creep tested in vacuum at high stress levels. The stable precipitates contained little or no tungsten or tantalum. Hafnium carbide at a concentration of about 2 mole % was the most effective addition. Other compounds produced effects according to their absolute melting points. A ratio of metal to nonmetal of 1.3 yielded the best properties. An empirical creep-rate equation was established which took into account the several variables and gave a hyperbolic sine stress dependence. On this basis a new equation for predicting the 100-hr rupture stress was determined.

Japanese investigators[86] found that strain-rate dependence of the flow stress of Nb–26 at.% Zr alloy was larger than that of pure niobium at all temperatures from 201 to 573°K. Above room temperature the strain-rate dependence of niobium disappears, but that of the alloy is still significant. At 77°K the alloy deforms by twinning and the flow stress becomes insensitive to the strain rate. The results of this study indicate that the rate-controlling mechanism for the flow of the alloy is the same as that for pure niobium. Assuming that the double kink formation is the rate-controlling process, the kink energy of the alloy was determined to be about 1.25 ev, which is nearly three times larger than that for niobium.

Bureau of Mines researchers[87] combined niobium and tantalum with selected alloying elements to achieve solid solution and dispersion strengthening. Fifty-six alloys were evaluated to determine their formability, hardness, strength at elevated temperatures, and oxidation resistance. The following six alloys showed high-temperature strength: Nb–15 Hf–5 W–2 Zr–4 Al–4 Ti–2 N, Nb–15 Hf–5 W–5 Zr, Nb–15.3 Ti–4.1 Zr–13.7 Hf, Ta–20 Hf–4 Al, Ta–30 Hf–4 Al, and Ta–20 Hf–5 W–4 Al. At 1200°C the niobium alloys exhibited strength values of 40,000 psi or greater, and the tantalum alloys had strength values from 50,000 to 58,000 psi. For a 2-hr oxidation-test period at 1000°C, weight gains of only 9 and 8 mg/cm$^2$, respectively, were observed for Nb–15 Hf–5 W–2 Zr–4 Al–4 Ti–2 N and Ta–20 Hf–5 W–4 Al.

German investigators described a kinetic model for use in interpretation of results obtained from investigations of the Nb–O system.[88] Their investigations show that tentative pressure–temperature–composition phase diagrams of the Nb–O system should be based on the assumption that the important components of the gas phase are niobium, NbO, and $NbO_2$ molecules; whereas the oxygen pressures measured in steady-state experiments do not affect the thermodynamic equilibrium.

The effect of oxygen content on the strain-aging behavior of electron-beam-refined niobium has been studied, using both yield-point-return and internal-friction measurements.[89] The strain-aging index, given by $\Delta\sigma_y = \Delta\sigma_f + 2\,K_y d^{-\frac{1}{2}}$, has been found to be proportional to the amount of oxygen migrating from free solid solution. The dislocation-locking parameter $k_y$ attains a saturation value that increases with increasing initial oxygen content but is smaller than that for the annealed material. The results indicate that the smaller value of $k_y$ is primarily due to the increased density of dislocations in the strain-aged material. The increase in flow stress, $\Delta\sigma_f$, commences to become greater only after the $k_y$ parameter is almost saturated, and is associated with oxygen atoms that migrate to

dislocations beyond the saturation of Cottrell atmospheres.

Resistivity measurements have been used by German researchers to determine isothermal strain aging of oxygen-doped niobium and tantalum.[90] Samples were deformed by rolling at room temperature and were then aged in silicone oil at 140 to 200°C. It was shown that an inhomogeneity of dislocation distribution influenced strain-aging kinetics and was also responsible for deviations from Matthiessen's rule in that the observed decrease in resistance was smaller when measured at 293°K than at low temperatures. Evidence for the existence of equilibrium Cottrell atmospheres was shown. Measurements on aged samples deformed a second time were in agreement with Hahn's theory of the yield point.

At the University of Pretoria,[91] dislocation-velocity measurements have been made in high-purity molybdenum single crystals as a function of stress at 77 and 300°K by the etch-pitting technique. The results were compared with data obtained from strain-rate-change experiments at 77, 180, 300, and 575°K in the macrostrain region ($\epsilon > 10^{-3}$) and at 300°K in the microstrain region ($\epsilon \leqslant 10^{-3}$). All the experimental observations and the calculated deformation parameters were shown to be self-consistent on the basis that dislocation mobility is controlled by the nucleation of double kinks to overcome Peierls–Nabarro hills. The results also indicate that the same rate-controlling mechanism is operative in both the micro- and macrostrain regions and that the usual assumption that the mobile dislocation density does not change during a rapid strain-rate change is valid.

Creep correlations for body-centered cubic refractory metals have been made at Lawrence Radiation Laboratory.[92] The following empirical relation was developed:

$$\dot{\epsilon}_m = A\left(\frac{\sigma}{E}\right)^5 D$$

where $\dot{\epsilon}_m$ = the minimum creep rate
$A$ = a constant
$\sigma$ = the applied stress
$E$ = the average elastic modulus at the test temperature
$D$ = the self-diffusion coefficient

This relation is generally applicable for strain rates of less than $10^{-5}$/sec and temperatures greater than about one-half the melting point in absolute units. Creep data for all six bcc refractory metals were analyzed and compared with the creep properties of fcc, hcp, and bcc metals. In general, the deformation behavior of all the refractory metals, except possibly that of tungsten, can be represented by the above relation. This correlation is strong evidence of the similarity that exists between creep of pure close-packed metals and creep of pure bcc metals.

An investigation of the V–Tc alloy system has been conducted at Oak Ridge.[93] In addition to the terminal phases, three intermediate phases were observed. One phase is centered about 50 at.% technetium having the ordered bcc structure and two phases of higher technetium content exist above 1150°C. The structures of these phases were not determined, but it was proposed that they are also related to a bcc lattice. In addition to this work, researchers at Aerojet-General have made revisions to the V–C and Nb–C binary systems.[94]

A major revision to the Ti–W phase diagram has been proposed by investigators at Aerojet-General.[95] This diagram, shown in Fig. III-18, presents a solid-solution type rather than the previous peritectic type

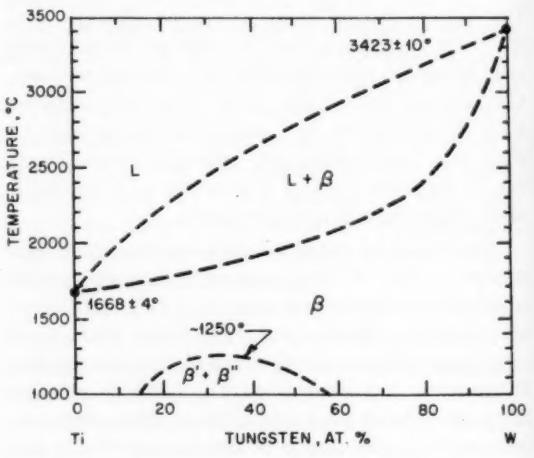



**Fig. III-18 Ti–W phase diagram as determined at Aerojet-General.[95]**

of alloy system. No phase discontinuity could be detected, and analysis of alloys quenched at solidus temperatures revealed only a single phase. The discrepancy between this work and the results of previous investigations concerning the high-temperature phase equilibrium of this system was attributed to insufficient homogenization of the alloys after arc melting.

(J. H. Peterson)

# Metallurgy of Common Cladding and Structural Materials

## Aluminum and Magnesium Alloys

The minimum creep rate of compacted magnesium powder containing 1 wt.% oxygen was found to be significantly lower at 450°C than that of magnesium alloys[96] containing aluminum, manganese, or zirconium, as shown in Fig. III-19. The low creep rate of

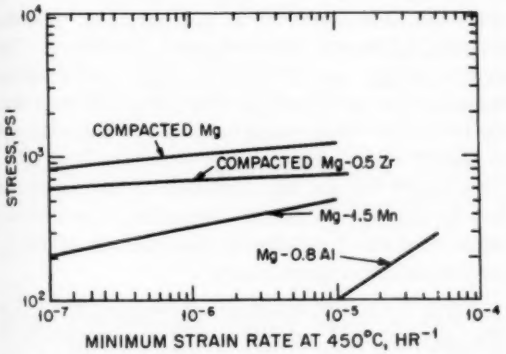



**Fig. III-19 Comparative creep strengths[97] of AL-80 (Mg–0.8 Al), AM-503 (Mg–1.5 Mn), compacted Mg–0.5 Zr, and compacted magnesium at 450°C.**

the oxygen-containing compacts was attributed to the presence of MgO particles at the grain boundaries. These particles reduced grain-boundary migration processes, restricting both intergranular slide and intergranular shear. Diffusion creep was found to be inoperative in the compacted material.

The primary creep of Magnox AL-80 at 450 to 620°C can be described by[97]

$$\epsilon = 3.2 \times 10^5 \, \sigma^{4.5} \, t^{0.7} \exp(-32{,}000/RT)$$

and it is suggested that a function of grain size may be incorporated such that

$$\epsilon = 1.2 \times 10^3 \, d^{-1.5} \, \sigma^{4.5} \, t^{0.7} \exp(-32{,}000/RT)$$

where $\epsilon$ = primary creep strain, %
$d$ = mean grain diameter at end of primary creep stage, in.
$\sigma$ = stress, psi
$t$ = time, hr
$R$ = gas constant = 1.98 cal/(mole)(°K)
$T$ = temperature, °K

The primary creep strain at a particular time is related to the secondary creep rate. Approximate values of the secondary creep rate of Magnox AL-80 may be derived from short-term primary creep tests by application of the equation

$$\dot{\epsilon} \approx 0.23 \, \epsilon^{0.5} / t$$

where $\dot{\epsilon}$ is the secondary creep rate, %/hr.

## Zirconium Alloys

Hot-rolling experiments were conducted[98] to define the causes of surface cracking in Zircaloy-4 during rolling at 795°C. To prevent surface oxidation during rolling, specimens were jacketed in mild steel, which was removed mechanically after rolling. It was found that strips that had been rolled by a 20-pass schedule exhibited inhomogeneous deformation with transverse corrugations. Strips that had been reduced by 5 passes did not have such corrugations. Those rolled at 20 passes contained bands of material with a crystallographic orientation different from that of the rest of the strip. Local thinning was also noticeable where the bands intercepted the surface. It is postulated that the positions at which banding occurs may depend upon localized differences in composition, crystallographic orientation, residual-stress distribution, dislocation densities, and grain size.

Empirical kinetic equations have been derived to describe the recovery of cold-worked Zircaloy-4 plate and tubing[99] at 550 to 1020°F (288 to 549°C). Samples that contained from 15 to 78% cold work were heated at temperature for up to 4000 hr. Figure III-20 illustrates the recrystallization of 78% cold-worked tubing in three directions as a function of temperature. The annealing process was found to take place as follows: (1) a dislocation climb and annihilation process to the limit allowed by the size of the deformation subcells, (2) a reorientation of the subgrain material into a recrystallization texture, (3) a growth of reoriented cells located in the most highly worked bands, and (4) a consumption of less favorably strained and/or oriented cells by the high-angle boundaries of the reoriented cells. Comparison of 15 and 73% cold-worked tubing showed the activation energy to be less (21 kcal/mole compared with 60 kcal/mole) and the subcell greater (8000 A compared with 1000 A) for the 15% cold-worked material.

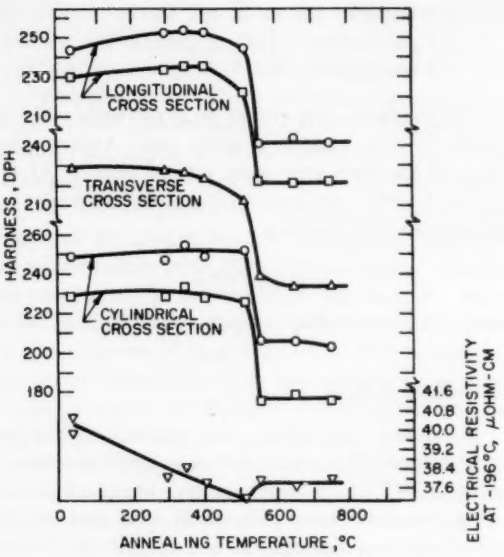



**Fig. III-20 The effects of annealing for 4 hr on the microhardness of 78% cold-worked Zircaloy-4 tubing.[99] ○, perpendicular to tube axis; □, parallel to tube axis; △, random; ▽, electrical-resistivity data.**

Theoretical predictions have been derived to explain the supersaturation of hydrogen in Zircaloy.[100] It was shown that precipitation of hydride platelets was inhibited by the stresses which would result from the volume increase due to formation of hydride platelets. An equation derived from a thermal-cycling model predicts values of hydrogen concentration as a function of the number of cycles. These results agreed well with the data of Westerman.[101] The dissolution of ZrH platelets in Zircaloy-4 was found to be very rapid at high temperatures.[102] It was observed that for hydrogen contents of up to 200 ppm the dissolution time at a temperature sufficiently above the phase boundary was given by

$$t \approx 1.65\, h^2 \exp(24{,}900/RT) \text{ sec}$$

where $h$ is the thickness of the ZrH platelet.

Soviet investigators[103] have found that the maximum amount of hydrogen precipitation in zirconium held under a thermal gradient occurs at about 245°C as illustrated in Fig. III-21. A zirconium specimen with a uniform hydrogen concentration was used to initiate the experiment, and the changes in hydrogen concentration after exposure to a thermal gradient were established by metallographic and chemical analyses.

Research is continuing at General Electric[104] to develop a zirconium-base alloy having nuclear properties better than those of Zircaloy-2. Extensive tests are being carried out on Zr–2 Cr–0.15 Fe, which has shown excellent corrosion resistance to pure water at 300°C. Burst- and tensile-test results at room temperature indicate that the alloy is stronger but less ductile than Zircaloy-2. However, the stress-rupture performance of the alloy at 400 to 600°C is poorer than that of Zircaloy-2. The small grain size (ASTM 10 compared with ASTM 7 for Zircaloy-2) of the Zr–Cr–Fe alloy may reflect its performance relative to Zircaloy-2.

Zirconium-alloy development is also being conducted by the Indians.[105] Additions of chromium to zirconium have resulted in strengthening, whereas niobium additions improved work hardening. The highest strength was obtained by adding both niobium and chromium to zirconium. The strength increase was not evident in the annealed material but was obtained by quenching and tempering as shown in Table III-6. The strength increase was attributed to the martensite that formed on quenching. Annealing temperatures higher than 500°C resulted in precipitation of $ZrCr_2$ and destruction of the martensite.

Creep tests have also been performed on Zr–0.5 Nb–1.0 Cr in air[106] at 300 to 470°C with stresses of 30,000 to 75,000 psi. It was found that in this temperature range the alloy exhibited creep properties superior to those of Zircaloy-2 and comparable to those of Zr–2.5 Nb. The effects of oxygen content and quenching temperature on the amount of prior alpha in Zr–2.5 Nb have been determined.[57] The percentage of

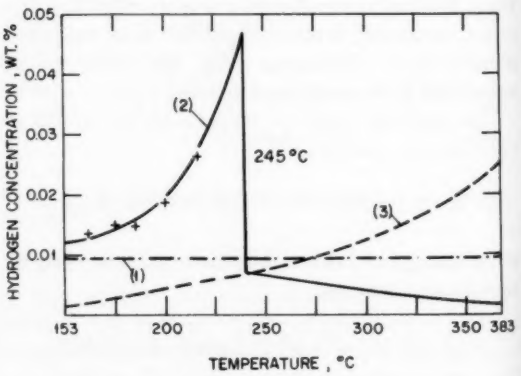



**Fig. III-21 Hydrogen migration in zirconium resulting from a thermal gradient.[103] (1) Initial hydrogen concentration; (2) final hydrogen concentration; (3) limiting solubility of hydrogen in alpha zirconium.**

**Table III-6 Effect of Heat-Treatment on the Room-Temperature Tensile Properties of the Zirconium Alloys[105]**

| Alloy composition (balance zirconium), wt.% | Heat-treatment | Yield strength, 1000 psi | | Ultimate tensile strength, 1000 psi |
|---|---|---|---|---|
| | | 0.1% offset | 0.2% offset | |
| 3.5 Nb | Annealed at 850°C for 1 hr and furnace cooled | 40.2 | 42.1 | 60.5 |
| 1.0 Cr | Annealed at 850°C for 1 hr and furnace cooled | 37.4 | 40.2 | 60.5 |
| 1.0 Cr–0.5 Nb | Annealed at 850°C for 1 hr and furnace cooled | 37.4 | 42.3 | 59.0 |
| Zirconium (sponge) | Annealed at 850°C for 1 hr and furnace cooled | | 32.4 | 43.1 |
| 0.5 Nb | Beta quenched from 900°C | 45.0 | 50.9 | 71.9 |
| 1.0 Cr | Beta quenched from 900°C | 68.0 | 74.3 | 104 |
| 0.5 Nb–1.0 Cr | Beta quenched from 900°C | 64.2 | 75.3 | 146 |
| 0.5 Nb–1.0 Cr | Beta quenched from 900°C and tempered at 300°C for 24 hr | 56.7 | 66.7 | 130 |
| | Tempered at 400°C | 84.4 | 97.8 | 138 |
| | Tempered at 500°C | 70.0 | 86.8 | 144 |
| | Tempered at 600°C | 60.6 | 72.1 | 106 |
| | Tempered at 700°C | 49.1 | 52.7 | 73.7 |

prior alpha phase was observed to increase with both decreasing quenching temperature and increasing oxygen content.

Transformation characteristics of Zr–Cu alloys upon quenching from the beta phase have been studied by the French.[107] Figure III-22 illustrates the TTT curve for Zr–2.4 Cu quenched from 960°C. Fast quenching rates result in martensitic transformation of an omega phase which has a hexagonal structure, whereas intermediate quenching rates result in omega-phase zirconium, alpha-phase zirconium supersaturated with copper, and possibly $Zr_2Cu$. Slow cooling rates result in alpha zirconium and particles of $Zr_2Cu$. Decomposition of the omega phase occurs at 418 to 455°C.

In a Zr–3 vol.% $Y_2O_3$ dispersion, chemical reactions were found to increase with increasing sintering times and temperatures.[108] The reaction was not predicted thermodynamically for the Zr–Y–O system. The yttria particles tended to minimize grain growth and inhibit recovery and recrystallization of worked material. Additions of greater than 2 vol.% $Y_2O_3$ resulted in significant improvements in rupture times and reductions in minimum creep rate[109] as shown in Fig. III-23. The dispersed particles are believed to affect the rupture properties by restricting the shear and migration of grain boundaries.

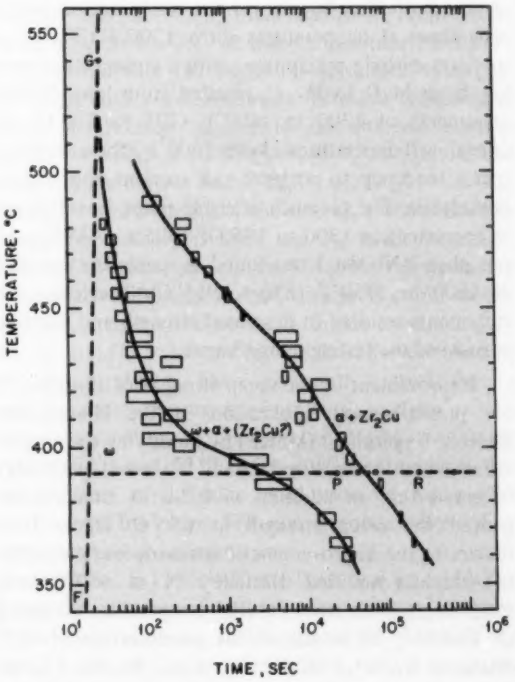



Fig. III-22 Transformation curves[107] for Zr–2.4 Cu quenched from 960°C.

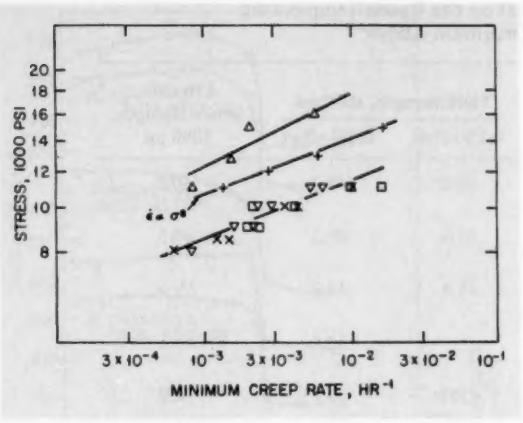
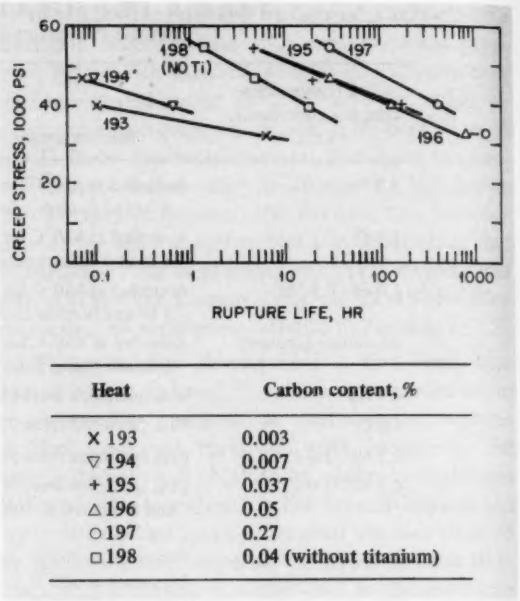



**Fig. III-23 Minimum creep rates for sintered $Zr-Y_2O_3$ dispersions.[109] $Y_2O_3$ additions: △, 5 vol.%; +, 3 vol.%; □, 2 vol.%; X, 1 vol.%; ▽, 0 vol.%.**

## Stainless Steels and Nickel-Base Alloys

An evaluation of Hastelloy X as a nuclear cladding has been summarized by researchers at Aerojet-General.[9] Their main conclusion was that the microstructure of Hastelloy X was not stable if annealed for long times at temperatures above 1300°F (705°C). A uniform carbide precipitate, with a composition varying from $M_4C$ to $M_{12}C$, resulted from long thermal treatments at 1300 to 1600°F (705 to 870°C). At annealing temperatures above 1600°F, these particles had a tendency to coalesce and reorient at the grain boundaries. The presence of sigma phase was detected in specimens at 1300 to 1450°F (705 to 790°C), and mu phase ($Ni_7Mo_6$) was found in specimens annealed at 1600 to 1750°F (870 to 955°C). The long heat-treatments resulted in decreased strength and ductility at most of the testing temperatures.

Improvement of the creep strength of Hastelloy N for pressure-vessel application in the Molten Salt Reactor Experiment (MSRE) by modifying the composition is still being investigated.[10b] It was previously observed that an addition of 0.5 wt.% titanium improved the creep strength at 650°C. Figure III-24 illustrates the improvement of stress-rupture properties of titanium-modified Hastelloy N at 650°C with increasing carbon content. High-temperature annealing of Hastelloy N results in the precipitation of $M_6C$ phases as $Ni_3Mo_3C$ in the matrix and $Ni_2Mo_4C$ at the grain boundaries. Increase of silicon content in the alloy caused large increases in the silicon content of the carbide precipitates.




| Heat | Carbon content, % |
|---|---|
| X 193 | 0.003 |
| ▽ 194 | 0.007 |
| + 195 | 0.037 |
| △ 196 | 0.05 |
| ○ 197 | 0.27 |
| □ 198 | 0.04 (without titanium) |

**Fig. III-24 Effect of carbon on the rupture life[10b] of modified Hastelloy N at 650°C.**

## Pressure-Vessel Steels

Long-time stress-rupture tests were conducted on 10 different steels in both the quenched-and-tempered and the normalized condition.[110] It was found that the rupture life was longest for quenched-and-tempered specimens at lower testing temperatures, whereas normalized steels exhibited longer rupture lives at higher testing temperatures. Welding was found to reduce the strength of AS17E, AS17F, AS17A, and A542, whereas the strength of the other steels was unaffected by welding. It was not possible to correlate the response of notched specimens to composition, microstructure, or smooth-bar properties.

Long-time (up to 20,000 hr) creep-rupture properties of 12 wt.% Cr–Mo–V–Nb steel at 500 and 550°C were found to depend on the initial tempering temperature and carbon and boron contents.[111] The properties were changed by dissolution of precipitates (fine $M_2X$) and their subsequent agglomeration as $M_{23}C_6$ during the long time at temperature. It was observed that a high tempering temperature (700°C or above), a low carbon content (<0.10 wt.%), and a high boron content (0.006 wt.%) resulted in improved creep properties.

(M. Kangilaski)

# Diffusion

The Diffusion Information Center in Cleveland, Ohio, has been publishing *Diffusion Data,*[112] a periodical that gives a continuous compilation of references on diffusion since 1967. The compilations include references on diffusion in solid and liquid metal and alloy systems, diffusion in intermetallic compounds, ceramics, glasses, and miscellaneous systems, and permeation of gases into and through solids and liquids. A compilation of all diffusion data published prior to 1967 is planned for publication as a special volume.

A number of bibliographies have appeared in the literature which will further assist those involved in investigations of diffusion behavior. A selected bibliography of ionic self-diffusion in simple oxides has been compiled by Harrop.[113] Activation energies, frequency factors, and temperature ranges are tabulated for specific elements diffusing into the oxide. A similar bibliography by Askill[114] also contains a number of systems and references, specifically impurity diffusion in oxides. Along with Harrop's and Cumming's earlier bibliography,[115] these listings offer a fairly complete reference of currently available data on the diffusion in oxides. In addition, the National Bureau of Standards[116] has tabulated diffusion constants for various systems. Frequency factors and activation energies are given for the diffusion in the borides, carbides, and oxides of Be, Hf, Mo, Nb, Ta, Th, Ti, and Zr and for diffusion of C, N, and O in these metals and some of their compounds. A similar list of data is being compiled for uranium compounds.

Kelly[117] has developed a correction for Fick's second law of diffusion which was considered unsatisfactory since it permits some of the diffusing particles to travel at speeds relatively faster than the free-space speed of light. An analysis was based on the covariant form of the Boltzmann equation which produced a more satisfactory relativistic diffusion equation to describe the required casual behavior.

The concept of an effective binary diffusion coefficient (EBDC) was evaluated[118] to describe diffusion of a species in systems containing three or more components, two of which are independently variable. The use and limitations of the EBDC were considered in the cases of steady-state diffusion, the unsteady state with infinite and semi-infinite couples, and a unidirectional unsteady state with finite diffusion lengths.

Correlation of the activation energy of self-diffusion in metals with the atomic-bond parameter and the activation volume for self-diffusion have been evaluated.[119] It was suggested that differences in activation-energy values for solute diffusion and self-diffusion can be attributed to the differences in cohesive-bond parameters if a depletion or contribution of valence electrons by solutes occurs and changes the Fermi energy of the solvent. In the case of diffusion of nontransition elements in noble metals, an increase in the Fermi energy of the solvent reduces the binding energy which thereby decreases the activation energy for diffusion. The converse is postulated for transition-element diffusion in noble metals. However, this model does not appear to give good correlation when compared with existing diffusion data for self-diffusion and tracer diffusion of transition elements in noble metals.

Anomalous values for the activation energy and frequency factor for surface self-diffusion were analyzed,[120] and a theory was developed to explain these discrepancies. Two mechanisms for surface diffusion in face-centered cubic metals were indicated using a terrace-ledge-kink model. At high temperatures the resulting diffusion constants agreed well with the adatom mechanism in that diffusion occurs over terraces in the surface. At low temperatures, diffusion is associated with the migration of surface vacancies. The high- and low-temperature diffusion constants in these metals were related to the absolute melting point: for $T/T_m > 0.75$, $Q_s = 30\ T_m$ kcal/mole and $D_0 = 740$ cm$^2$/sec; for $T/T_m < 0.75$, $Q_s = 13\ T_m$ kcal/mole and $D_0 = 0.014$ cm$^2$/sec. $Q_s$ is the activation energy for surface diffusion and $D_0$ is the frequency factor. Only one mechanism was observed operating for surface diffusion in body-centered cubic metals which is characterized by the diffusion constants $Q_s = 19\ T_m$ and $D_0 = 3.6$ cm$^2$/sec, at least for diffusion at low temperatures. These constants suggest that a surface-vacancy mechanism is at work in these metals. The identification of impurity effects by correlating values of the surface diffusion coefficient with relative temperatures of diffusion was discussed, along with mechanisms by which diffusion is either enhanced or suppressed by these impurities.

Diffusion in zirconium, its alloys, and its oxides has been the subject of several investigations. Oxygen diffusion in zirconium, making use of the $^{16}O(d,p)^{17}O$ nuclear reaction, was described by French investigators.[121] Energy spectra of protons obtained experimentally were compared with spectra calculated on a theoretical basis. The oxygen-concentration profile in

zirconium and in a Zr–Cu alloy after an oxidizing treatment at 750°C was measured. The results showed that the relation of microhardness to oxygen content is not linear and that the diffusion coefficient of oxygen in zirconium is dependent on concentration. A Cu–Mo–Zr alloy was subjected[122] to diffusion annealing in close contact with magnesium at 510°C for 1000 hr. Diffusion penetration of magnesium led to total embrittlement of the alloy, whereas the tensile strength and the yield point were decreased by 25 and 11%, respectively.

A study of the electromigration of oxygen, carbon, and nitrogen in zirconium is being conducted by Ames Laboratory.[42] The movement of the interface between sections of a rod with high and low oxygen and carbon contents was traced at different temperatures, and the migration velocities of the solutes were determined. Oxygen was added to the zirconium as $ZrO_2$, and the concentration profile was determined by vacuum-fusion analysis. The migration velocity of oxygen in zirconium was found to be 1.0, 1.1, and 2.7 mm/hr at 1625, 1700, and 1800°C, respectively. The migration of carbon was traced by doping the zirconium rod with $^{14}C$ and determining the beta activity with a low-beta radiation counter. At 1800°C a migration velocity of 0.25 mm/hr was found for carbon. Additional experiments are being conducted to measure the movement of carbon at 1625 and 1700°C.

Oxygen-ion diffusion in $ZrO_{2-x}$ was determined[123] by measurements of the oxide growth rate on zirconium samples exposed to oxygen at 700, 750, 800, and 850°C up to 250 hr. It was assumed that the diffusion coefficient for oxygen in alpha zirconium was $5.4 \exp(-50{,}800/RT)$ cm$^2$/sec as previously observed by Kearns and Chirigos.[124] The oxygen concentration at the surface of zirconium oxide was also assumed to correspond to that in $ZrO_2$. The oxygen concentration initially was $9.3 \times 10^{-4}$ g/cm$^3$ in zirconium. A least-squares analysis of the data, including independent measurements at 600°C by Hussey and Smeltzer[125] resulted in the Arrhenius-type equation $D = 2.88 \times 10^{-4} \exp(-28{,}400/RT)$ cm$^2$/sec for the temperature range 600 to 850°C.

Self-diffusion in zirconium and hafnium and diffusion of $^{95}Nb$ in alpha zirconium were investigated by Argentine researchers.[126] They also determined new data for self-diffusion in titanium. The temperature dependence of diffusion of the various isotopes in alpha zirconium is shown in Fig. III-25, and similar results for self-diffusion in alpha hafnium are given in Fig. III-26. Diffusion constants determined for $^{44}Ti$ in 99.99 wt.% titanium between 700 and 850°C were

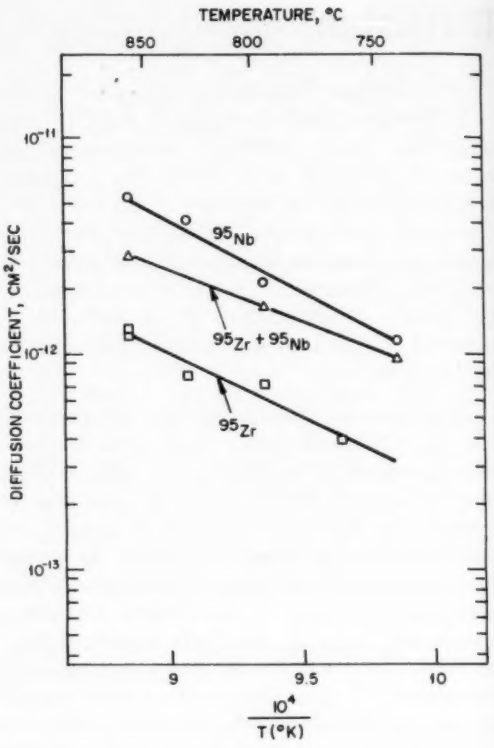



**Fig. III-25 Temperature dependence of diffusion of $^{95}Zr$, $^{95}Zr + {}^{95}Nb$, and $^{95}Nb$ in hcp zirconium.[124]**

established as $8.6 \times 10^{-6}$ cm$^2$/sec for the frequency factor and 35,900 cal/mole for the activation energy. Previous experiments and explanations concerned with the anomalous diffusion behavior in these metals were reviewed, and it was suggested that the same mechanism producing anomalous behavior in the beta phases (body-centered cubic) of these metals also operates in alpha phases (hexagonal close packed). This mechanism occurs either by itself or in combination with a second mechanism operating in the higher temperature region.

A number of diffusion studies conducted by Ames Laboratory during the past year were summarized.[42] The diffusion of carbon, oxygen, and nitrogen in beta thorium was determined[42b] between 1440 and 1715°C. The results were given by the following temperature-dependent equations:

$$D_{C \text{ in } \beta\text{-Th}} = 2.2 \times 10^{-2} \exp(-27{,}000/RT) \text{ cm}^2/\text{sec}$$

$$D_{N \text{ in } \beta\text{-Th}} = 3.2 \times 10^{-3} \exp(-17{,}000/RT) \text{ cm}^2/\text{sec}$$

$$D_{O \text{ in } \beta\text{-Th}} = 1.3 \times 10^{-3} \exp(-11{,}000/RT) \text{ cm}^2/\text{sec}$$

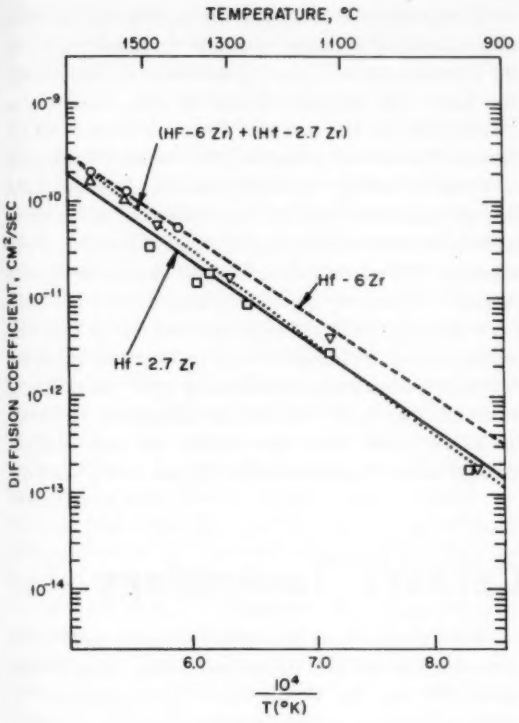



Fig. III-26 Temperature dependence of diffusion of $^{175}Hf$ + $^{181}Hf$ in hcp hafnium.[124]

The mobility and diffusion coefficients for carbon, nitrogen, and oxygen in lutetium at 1330, 1450, and 1700°C were also measured[42c] by chemical analyses (for nitrogen and oxygen) and by $^{14}C$ tracer techniques (for carbon). The interstitials moved in the direction of electron flow when a d-c current was applied to the lutetium rod. Diffusion of oxygen in rare-earth oxides was studied[42d] by a thermobalance technique by which the rates of weight gains of substoichiometric oxides were determined. Results of cation diffusion in the rare-earth oxides are also determined.[42e] Radioactive-trace techniques established that $^{91}Y$ diffuses into $Y_2O_3$ according to relation $D = 1.65 \times 10^{-2} \exp(-69{,}200/RT)$ cm²/sec, whereas for $^{169}Er$ in $Er_2O_3$, the relation was found to be $D = 1.48 \exp(-102{,}200/RT)$ cm²/sec.

A bibliography on the permeation and diffusion of nitrogen, oxygen, and rare gases through stainless steel has been prepared by Los Alamos.[127] Some 24 pertinent abstracts were found in a search of *Chemical Abstracts, Nuclear Science Abstracts,* and the *Review of Metal Literature* from 1947 to date.

Uranium diffusion in $ThO_2$ and in a $ThO_2$–$UO_2$ solid solution was investigated by $^{237}U$ tracer techniques.[128] Diffusion of $^{237}U$ in $ThO_2$ was determined between 1800 and 2000°C, and diffusion of $^{237}U$ in a $ThO_2$–$UO_2$ solid solution was examined at temperatures of 1800 to 2300°C. Penetration data were obtained by serial sectioning and measuring residual activity of the gamma spectrum of $^{237}U$ by X-ray spectrometry. Lattice-diffusion contributions near the surface were separated from the grain-boundary-diffusion effects by extrapolating the linear slope of the grain-boundary penetration-activity curve from the regions unaffected by lattice diffusion to regions near the surface. Lattice-diffusion coefficients derived by this technique were expressed by the following equations:

$$D_{\text{U in } ThO_2} = 1.10 \times 10^{-4} \exp(-76{,}400/RT) \text{ cm}^2/\text{sec}$$

$$D_{\text{U in } ThO_2-UO_2} = 7.59 \times 10^{-4} \exp(-85{,}900/RT) \text{ cm}^2/\text{sec}$$

Grain-boundary-diffusion coefficients were obtained using the equation of LeClaire[129] and resulted in the following expressions:

$$D' \times 2a_{\text{U in } ThO_2} = 2.35 \times 10^{-9} \exp(-47{,}900/RT) \text{ cm}^3/\text{sec}$$

and

$$D' \times 2a_{\text{U in } ThO_2-UO_2} = 1.04 \times 10^{-7} \exp(-64{,}200/RT) \text{ cm}^3/\text{sec}$$

where $D'$ is the coefficient associated with grain-boundary diffusion and $2a$ is the grain-boundary width.

Lattice and grain-boundary diffusion at 600 and 1300°C have also been studied[130] with $^{59}Fe$ in stainless steels having grain sizes of about 50 $\mu$ or ranging from 2000 to 4000 $\mu$. Lattice diffusion predominated in the coarse-grained material, especially above 900°C where grain-boundary diffusion effects were nil. Lattice diffusion above 900°C was expressed by the equation $D = 1.74 \exp(-67{,}900/RT)$ cm²/sec. Below 900°C, evidence existed that dislocation pipes contributed short-circuit paths for diffusion. In the fine-grained material, grain-boundary diffusion predominated between 600 and 900°C and was described by the relation $D' \times 2a = 8.3 \times 10^{-7} \exp(-43{,}000/RT)$ cm³/sec. (A. N. Ashurst)

# Concrete

A study of the time-dependent strains in stressed and unstressed concrete heated at temperatures up to 290°F (140°C) was conducted by the U. S. Bureau of Reclamation.[131] Concrete prepared using type V cement and amphibole schist aggregate (1½-in. max.) was molded into cylinders 6 in. in diameter by 16 in. long which were fog-room cured for 1 month, then cured in air (50% relative humidity) at 73°F (23°C) for an additional month before testing. These specimens were loaded in uniaxial compression to 800 psi at room temperature and heated to 130, 180, 230, and 290°F (55, 80, 110, and 145°C); strains were then measured as a function of time up to 180 days. Similar strains were measured in stressed specimens (800 psi) maintained at room temperature and in unstressed specimens maintained at room temperature and 130, 180, 230, and 290°F. Results of this study are given in Fig. III-27.

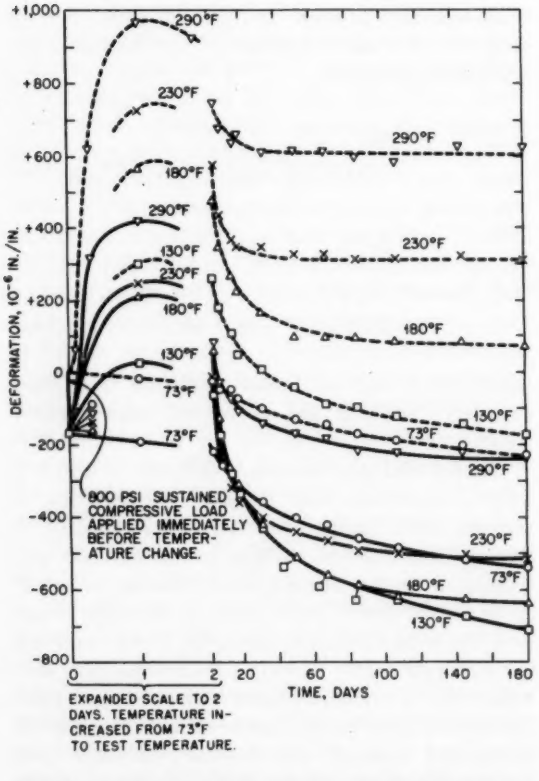



**Fig. III-27 Deformations of concrete with and without sustained loads.[131] Dashed lines denote concrete not under load; solid lines denote loaded concrete.**

The magnitude and even the sign of the deformations occurring in heated concrete were dependent on the temperature level, heating rate, external stress level, and time. The complex nature of the situation was underscored by the fact that there are as many as six factors that can contribute to the overall deformation observed, including: (1) drying shrinkage related to the loss of evaporable water, (2) reversible elastic deformations associated with normal thermal expansion of the aggregate, (3) irreversible deformations associated with thermal expansion of the hydrated-cement phase, (4) reversible elastic deformations associated with the instantaneous application of external stress, (5) time-dependent deformations associated with the presence of an external stress, and (6) time-dependent deformations associated with the change in mineralogical makeup of the hydrated-cement phase during heating.

(D. R. Lankard)

# Ceramic Technology

The mechanisms by which fibrous insulations attenuate the transfer of thermal energy were investigated by the Air Force Materials Laboratory.[132] Dynaquartz (heat-stabilized silica material), sapphire wool, and Dynaflex (alumina-silica fiber with chromia additive) were evaluated for their usefulness in the high-temperature environment. Effective thermal conductivities were measured in air, argon, and vacuum up to 2500°F (1371°C). Transmission experiments were carried out to evaluate the relative contribution of radiation-attenuation parameters for Dynaquartz.

It was found that measurement of the effective thermal conductivity of the three materials in air up to 2500°F could be carried out in a one-dimensional, guarded hot-plate apparatus with an accuracy of ±15%. At temperatures above 1500°F, radiation was the principal contributor to heat transfer in fibrous insulating materials. Gas conduction was the second largest contributor, but it can be effectively reduced by evacuation to moderate pressures. Solid conduction was of lesser importance in low-density fibrous insulations. The effective thermal conductivity of Dynaquartz may be predicted from estimates of the solid-conduction contribution, gas-conductivity data, and estimates of the absorption-scattering cross sections of the insulation. Measurements of the absorption and scattering cross sections can be used to guide the choice of insulation components at high temperatures where radiation is the principal heat-transfer mechanism. Because of the high contribution of radiation to

effective thermal conductivity, temperature gradients in the insulation will not be linear under steady-state heat-transfer conditions.

Wirth[133] has studied the sintering kinetics in the initial, intermediate, and final stages of sintering of ultrafine calcia-stabilized zirconia. Initial stage kinetics, as determined by isothermal-shrinkage studies, indicated that grain-boundary diffusion was operative. Since the activation energy in this stage agreed closely with that for oxygen-ion diffusion, this species apparently is rate controlling. Intermediate stage kinetics, observed by isothermal-porosity determination, indicated that oxygen-ion diffusion was still the rate-controlling mechanism. Material transport was postulated still to occur by grain-boundary diffusion, on the basis of the high ratio of grain-boundary volume to bulk volume. In the final stage, as observed by isothermal grain-growth studies, rate control apparently had changed to cation diffusion, on the basis of agreement of the activation energy for sintering and that for cation bulk diffusion.

Bennett et al.[134] examined the application of a microwave-stimulated electrodeless gas discharge to the sintering of $Al_2O_3$, BeO, $HfO_2$, MgO, and $ThO_2$. The apparatus is described, together with its method of operation. For $Al_2O_3$ and $HfO_2$, improved sinterability was attained. Specimens sintered by this method were mechanically better than conventionally sintered pieces from the same raw material. This effect resulted from easier attainment of the combination of small grain size and low porosity.

Young's modulus, fracture stress, and fracture strain of commercial alumina ceramics were determined at temperatures from −200 to 1200°C from bend tests by the Germans.[135] The influence of porosity, grain size, specimen diameter, and length on these properties was investigated. Bend tests were also made on commercially obtained magnesia, zirconia, and spinel ceramics in the same temperature range. Porosity ranged from about 4 to 20% and grain size varied from 5 to 60 $\mu$. Efforts to describe the combined effects analytically were limited to assuming the effect grain size had on strength and treatment of the observed porosity effect. On this basis the weakening influence of porosity was found to diminish with increasing temperature. As has been found by other investigators, no effect of grain size on Young's modulus was noted. The reduction in Young's modulus with increasing porosity was approximately independent of temperature. Refined bend tests of alumina-ceramic specimens indicated that Young's moduli in tension and compression are equal.

Diffusion mechanisms in ceramic oxides were reviewed by the Australians.[136] Methods of measurement also were discussed, and it was concluded that a simple correlation for cation self-diffusion based on structures does not exist.

Russian investigators have investigated phase relations in the $Cr_2O_3$–$TiO_2$ and $Cr_2O_3$–$ZrO_2$ systems.[137] Two eutectics (2153°K, 50 mole % $TiO_2$, and 2033°K, 96 mole % $TiO_2$) were found in the $Cr_2O_3$–$TiO_2$ system. The phase $Cr_2Ti_2O_7$ melts congruently at 2253°K. There are two high-temperature series of solid solutions, between 80 and 94 and 96 and 100 mole % $TiO_2$. In the system $Cr_2O_3$–$ZrO_2$, one eutectic at 39 mole % $ZrO_2$, melting at 2360°K, was found in accordance with Wartenburg's data.

(H. D. Sheets)

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Section

IV

Reactor Materials

# Special Fabrication Techniques

## Cast and Wrought Materials

### Melting and Casting Processes

The French[1] have patented an apparatus for the electron-beam melting and continuous casting of refractory materials such as UC. The apparatus consists of an electron gun mounted axially above the crucible, a device for supplying the material to be melted, rotating members for continuously replacing the crucible sidewall, and a means for rotating the complete crucible assembly to achieve better particle distribution at the surface of the melt.

Longitudinal and transverse sections of electron-beam melted and continuous-cast UC rods have been studied by microscopic methods.[2] A critical casting rate was identified which was due to the competition between crystals growing on nuclei on the rod surface and crystals formed in the liquid by homogeneous nucleation. It was noted that, in crystals without any privileged growing direction, the crystal size obtained had a minimum for a given casting rate. This minimum was explained by the combination of two competing phenomena: the nucleation rate and the disappearance of the smaller nuclei into the larger ones.

Oak Ridge investigators[3] found that contamination during electron-beam melting may be in part due to material volatilized from the chamber walls by the radiant energy of the beam. Thorough cleaning of the furnace chamber walls between melts improved the purity of electron-beam-melted niobium. Previous contamination from the chamber walls exceeded that from the emitter.

Combustion Engineering[4] has produced a high-purity V–15 Cr–5 Ti* alloy ingot weighing over 100 lb. The process steps included aluminothermic reduction of $V_2O_5$ to provide higher purity vanadium than is commercially available. The resulting vanadium derbies were double electron-beam melted to reduce the amounts of impurities, particularly interstitial elements. The ingot was then machined into chips that were compacted with high-purity chromium and titanium to form an electrode. Double arc melting of the electrode, first in argon and then in vacuum, resulted in a vanadium-alloy ingot with a total interstitial content of less than 400 ppm.

The Russians[5] have used a 60-kw electron-beam melting unit for the industrial production of ingots of Ti, Nb, Mo, Zr, Ta and their alloys which are up to 70 mm in diameter and 300 mm long. Electron-beam vacuum remelting increased the ductility and elongation and decreased the hardness of tantalum and niobium. For example, the hardness of niobium decreased from 85 to 65 kg/mm$^2$ after double remelting and to 52 kg/mm$^2$ after triple and quadruple remelting. The formation of very hard and brittle MoC and $Mo_2C$ occurs in the reaction of molybdenum with oil vapor; therefore production of ductile molybdenum requires the development of melting units with vacuum or diffusion pumps which use no oil or are equipped with special traps.

Crucibles for containing molten nickel and beryllium were developed and tested by Dow Chemical Company.[6] Dense, fine-grained crucibles made by hot pressing a variety of refractory compounds were tested for resistance to vacuum outgassing, thermal shock, and corrosion by molten beryllium and molten nickel. Heating rates up to 900°C/min were achieved by electron-bombardment heating in vacuum of $3 \times 10^{-5}$ torr. Titanium diboride was found to be a good container for molten beryllium, and a modified titanium carbide composition proved to be a satisfactory container for molten nickel.

### Fabrication of Cast Products

The French[7] have patented a process for producing clad metallic fuel elements. Composite billets or blooms of zirconium-clad Zr-2 to 8 U were first diffusion bonded at 750 to 950°C and then coextruded or rolled at room temperature to 400°C to form round bars, tubes, or plates. The method eliminates the necessity for preheating at high temperatures in con-

*Unless otherwise designated, all compositions are understood to be in weight percent.

trolled atmospheres and the use of sealing jackets prior to fabrication.

A British patent[8] describes an extrusion apparatus which incorporates a conventional cylinder, ram, and die, with a device for applying vibratory energy at a frequency of 20,000 cps, and a special conical tubular mounting member which is designed to minimize undesirable effects such as damping and frequency shifts. The hollow mounting member has a definite frequency of vibration and an acoustical length equal to an even integral number of quarter wavelengths of sound at the frequency of operation. This technique increases the extrusion rate and permits extrusion of difficult materials.

Metal fuel-element cans with external cooling fins have been directly extruded by the British.[9] A patent describes the heated segmental dies which are used in conjunction with a stepped or tapered mandrel which applies the extruding force. A means for disengaging the die segments after extrusion and a device for ejecting the extruded can are also described.

A nomogram developed by the British[10] gives the expected extrusion pressure for different materials, die angles, and extrusion ratios when the compressive stress-strain curve for the alloy is known. The theory and calculations leading to the nomogram are described, and a sample nomogram for many common materials is given. This nomogram applies only to round extrusions through a conical die.

Tantalum alloy T-111 has been deep drawn into a cup about 4 in. deep by 2 in. in diameter with a wall thickness of about 0.2 in. by Atomics International.[11] Aluminum bronze was found to be a satisfactory die material. Hardened steel was unsatisfactory because the large drawing forces necessary for the T-111 resulted in excessive contact between the T-111 and steel, thus tearing the T-111. Although multiple draws were needed, only one intermediate anneal at 2700°F (1480°C) for 1 hr was required. It was necessary to clean the die wash thoroughly from the T-111 blank between draws by caustic and acid pickles to avoid reaction with the alloy during annealing, which would cause embrittlement. (D. E. Stellrecht)

## Powder-Metallurgy Materials

Developments[12,13] in powder metallurgy have been reviewed by Battelle–Columbus. Progress in fabricating superalloy parts by powder-metallurgy techniques and an atomization process for producing superalloy powders are of particular interest. Yields of −40-mesh Udimet 700 and B-1900 powders were greater than 70%, and the oxygen content of the powders was maintained substantially below 300 ppm. Developments in the technology of slip casting of superalloys are also noted.

The status of powder metallurgy[14] in Poland has been reviewed with particular consideration of metal-powder production and shaping. Progress in the manufacture of sintered structural parts, bearings, frictional materials, dispersion-strengthened materials, nuclear materials, and materials for special purposes is described. Important advances in fundamental research are cited, and the directions of development in different fields of powder metallurgy are indicated.

The Russians[15] have fabricated molybdenum tubes by hot pressing tubular blanks made by powder metallurgy. Processing was accomplished in conical or spherical dies at 220 to 340°C using graphite lubrication. Prior to hot pressing, as well as after each pressing pass, the billets were annealed in either hydrogen or vacuum. Optimum deformations per pass and optimum deformation rates are described.

British investigators[16] have fabricated sheathed ceramic fuel materials by hydrostatic extrusion. The method employs a die, a container for the pressurized fluid and for the fuel element to be extruded, and a means for pressurizing the fluid to drive the element through the die. Prior to extrusion, the fuel element is coated with a tenacious deformable coating to prevent direct contact with the die and to eliminate escape of pressurized fluid past the die during extrusion.

As part of their program to develop SAP alloys, Oak Ridge investigators[17] have determined the effects of transverse extrusion on the mechanical properties of SAP 895. Specimens from SAP 895 bar extruded before receipt at a 20:1 ratio were further extruded in a direction perpendicular to the original extrusion direction, with the transverse extrusion ratios ranging between 1.5 and 30:1. The extrusion temperature was about 500°C, and both shear dies and 45° conical dies were used. Results of tensile testing at 450°C on this material are plotted in Fig. IV-1. The strength increased rapidly with increasing transverse extrusion ratio and surpassed the initial longitudinal stress (11,000 psi) at a reduction ratio of about 8:1. The ductility was essentially restored by this amount of transverse working. This seems to be a more effective way of improving properties than is further longitudinal extrusion.

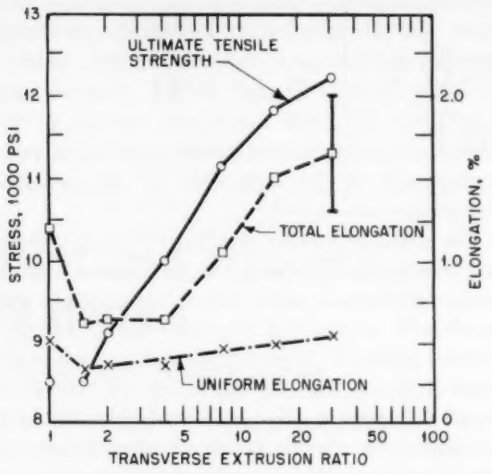



**Fig. IV-1 Tensile properties of SAP 895 after transverse extrusion at about 500°C (Ref. 17).**

A method of forming refractory-metal bodies containing dispersed refractory-metal carbides[18] has been developed at United Aircraft. Refractory metals such as Nb, Ta, Mo, W, Ti and their alloys in fine powder form are first coated with thin carbide shells in a fluidized bed. The powders are then warm or hot worked to fracture the shells and uniformly disperse the carbide phase throughout the structure.

(C. A. MacMillan)

# Pressure Bonding

Bonding procedures and diffusion characteristics for vanadium-clad zirconium were studied by Vermani, Murarka, and Agarwala.[19] This materials combination was intended as a possible cladding material for use in organic-cooled reactors. The bonding surfaces were first prepared by machining and abrading and then electropolished. Zirconium surfaces were electropolished in glacial acetic acid and a perchloric acid bath, whereas vanadium surfaces were electropolished in a 10% sulfuric acid bath. Bonding couples of the materials were heat-treated in purified helium ($\sim 0.5 \times 10^{-3}$ mm) at 400 to 1050°C for 1 hr. Metallographic examination of these couples showed very little diffusion in alpha zirconium at less than 800°C. Only one diffusion band, an apparent result of volume diffusion, was observed after bonding at 900 to 1050°C. Although no tests of bond strength were conducted, a bonding temperature of 950°C appeared most satisfactory. In view of the limited diffusion observed at the lower bonding temperatures, vanadium-clad zirconium was considered satisfactory for long-term reactor operation at about 400°C.

Researchers at Los Alamos[20] have evaluated joining of nuclear-grade graphite with intermediate foils of Zr, Ta, Mo, W, and Fe. Two types of joints were produced in this investigation: a diffused joint, which consisted of a carbide–carbon eutectic zone, and a continuous carbide joint. The experimental bonding conditions were achieved by induction-heating the graphite and foil assemblies in an argon atmosphere to temperatures up to 3000°C and maintaining a pressure of about 200 psi for 3 to 15 min. Diffused joints, which were formed at the higher temperatures for each system, exhibited elevated-temperature strengths superior to those of corresponding carbide joints. It was generally noted that increased bonding temperatures resulted in increased room-temperature flexure strengths of the bonds. The strongest continuous carbide joints in this study were produced with a zirconium intermediate foil.

A British patent[21] describing a method for pressure-bonding ceramic-to-metal gradient seals has been issued. The sealing region in the assembly consists of a mixture of the refractory metal and ceramic, with the composition varying according to the proximity of the faying surfaces. After a series of graded powder layers are deposited at the joining surfaces of the components, the assembly is pressure bonded to consolidate the powder and bond it to both the metal and ceramic components. Joining of niobium to $Al_2O_3$ was cited as an example of the usefulness of this method.

Tungsten-clad W–50 vol.% $UO_2$ cermet fuel assemblies for thermionic applications have been fabricated by gas-pressure bonding at Battelle–Columbus.[22] Fuel forms consisting of tungsten-coated $UO_2$ particles and fine (0.88 $\mu$) tungsten powder were first blended with a Parawax binder, die pressed, outgassed at 1500°C for 30 min, and then hot isostatically pressed to 92% of theoretical density in molybdenum containers at 2900°F (1595°C) and 10,000 psi for 3 hr. After the molybdenum was removed by acid leaching and grinding to final size, the fuel form along with arc-cast tungsten cladding components was heat-treated in hydrogen at 1750 to 1800°C for 1½ hr and then slow cooled (500°C/hr). All components were again assembled in a molybdenum container and pressure bonded at 3100°F (1705°C) and 15,000 psi for 3 hr. Prior to cooling, the autoclave was depressurized to permit relaxation of the

bonded assembly. Clad fuel pellets produced in this manner were capable of withstanding 100 thermal cycles to 2000°K without failure. (S. W. Porembka)

# Plating

## Nonelectrolytic Chemical Plating

Deposition of tantalum and iridium on quartz plates with previously deposited layers of carbon and $SiO_2$ was studied by Lainer and Kholmyanskii.[23] Thin films produced by vacuum evaporation were investigated by electron diffraction and electron microscopy. During condensation, tantalum oxidized and formed films of TaO which had a face-centered cubic lattice, and iridium films had the normal lattice of the bulk material. The crystal size as a function of the substrate temperature and the average film thickness were calculated from the broadening of the interference maxima.

The structure of tungsten films sputtered under $10^{-3}$ torr by argon ions at 1000 volts and condensed at a rate of 120 A/min on NaCl was investigated as a function of substrate temperature by Sella and Coppens.[24] Up to 190°C the films were amorphous; between 200 and 350°C they exhibited a body-centered cubic structure, whereas in the range 400 to 450°C the epitaxy structure became face-centered cubic. The effects of other parameters such as sputtering rate, pressure, and film thickness were also investigated.

Adherent metal coatings of Cd, Zn, Mg, Tl, Bi, Pb, and Ag up to 0.40 mm thick were deposited on metal substrates by means of two cathodes in a glow discharge at Mound Laboratory.[25] The samples to be coated were mounted on one of the cathodes. These samples were cleaned before and also during deposition by ion-bombardment sputtering. The other cathode contained the coating material in a tray that was thermally insulated from its support. The initial layers of the coating were deposited by bias sputtering, and the bulk of the coating was deposited at rates up to 0.015 mm/min when the coating material was evaporated. The method was defined as evaporation-abetted bias sputtering, with ion plating and bias sputtering being the physical processes involved. Coatings deposited by this method at 400°C adhered very well. Coatings deposited at 100°C adhered only moderately well, primarily because of low coating ductility at this deposition temperature.

Tungsten single crystals were prepared[26] by vapor deposition on single-crystal wires from $WCl_6$. The deposition temperatures were 1300, 2000, and 2700°C and deposition times were 1, 4, and 10 hr. The orientation of the rod axis in all experiments was near |1 1 0|. The exterior limiting planes were (1 1 0), (2 1 1), (1 0 0), and (1 1 1) at high supersaturation and (1 1 0) and (2 1 1) at low supersaturation. At high supersaturation the planes appeared macroscopically smooth, corresponding to the increased nucleation and reduced surface mobility. At low supersaturation the (2 1 1) and (1 1 0) planes showed a profile characterized by (1 1 0) steps. The size of the steps increased with lower supersaturation. Grain and subgrain boundaries of the substrate were continued into the deposited layer, and the number of dislocations diminished.

Experimental data and a laboratory apparatus for plating $Al_2O_3$ tubes with niobium were described by Fiebelmann.[27] Zinc was used for the reduction of $NbCl_5$ and the influence of pressure and temperature was examined. The main features of the deposited niobium layers were high chemical purity, good surface adherence even during sharp thermal cycles, and equal layer thickness. Brazing and diffusion bonding of niobium-plated $Al_2O_3$ bodies for applications in the range 800 to 1100°C was shown to be feasible.

A scaled-up apparatus for producing 1-ft lengths of 0.5-in.-diameter W–Re alloy tubing has been tested and modified at Lawrence Radiation Laboratory.[28a] Additional modification of the apparatus is required to provide greater control of mandrel temperature, feed-gas flow rate, and mandrel translation. Nevertheless, the room-temperature properties of rings taken from several sections of two of the three tubes were comparable with those previously reported for the 1-in.-long W–Re tubes. Fluorine analyses obtained on these standard 1-in.-long W–Re tubes prepared in the original apparatus indicated no apparent dependence of fluorine content on temperature, rhenium content, pressure, mole ratio of $H_2/MF_6$, $MF_6$ flow rate, or plating rate.

A study of thermionic-converter hot shells for application in a gasoline-fired thermionic power supply has been initiated.[29] Shells of SiC on tungsten indicated extensive problems as a result of thermal-shock cracking and separation of SiC from the tungsten substrate when heated at 1400°C for about 100 hr. To avoid these problems, various changes in the shell composition and deposition processes were considered and evaluated. A composite shell was developed which consisted of a machined graphite body 40 mils thick

with tungsten deposited on the inside and SiC deposited on the outside. The graphite is completely encapsulated and provides surfaces on which to vapor-form the SiC and tungsten; it also serves as a reaction barrier between the SiC and tungsten in the area heated by the burner. These composite shells were tested at Thermo Electron and showed considerable promise. In the preparation of the shells, tungsten was deposited by hydrogen reduction of $WF_6$, whereas the SiC was deposited by pyrolysis and/or hydrogen reduction of $CH_3SiCl_3$. (J. Zupan)

### Electroplating

An effective method for electropolishing uranium was developed by Dow technologists.[30] Surface smoothing by 40 to 60% was accomplished in 20 to 45 min with the removal of 20 to 46 $\mu$ (e.g., 51 to 20 $\mu$in., rms) at 13 volts in an ethanediol–sodium hypophosphite solution at 90°C. The initial cathode current density was 13 amp/sq ft.

Zirconium was electrodeposited on uranium in a pore-free condition up to a thickness of 5 mils at Battelle–Northwest[31] in a KF–LiF eutectic mixture containing 2 to 10 wt.% $ZrF_4$. The best cathode current density was in the range 20 to 40 ma/cm$^2$. The operating temperature was 625 to 675°C. Internal voids were observed in cross sections, but acid treatments revealed no pores exposing uranium. A layer of Zr–U interdiffusion alloy appeared to be dense. Zirconium coatings thicker than 5 mils showed a structural change from fine to coarse crystals, which was attributed to degradation of the molten salt or possibly the formation of insoluble $ZrF_3$ particles in the bath.

Thick ($10^{-3}$ cm) hydroxide films of U, Np, Pu, and Am are being deposited at cathode surfaces in acid solutions of the actinides with a potential of 12 volts between platinum anodes spaced 5 cm above the cathode.[32] The process is independent of the cathode material, but stainless-steel cathodes are customarily used with acid electrolytes such as: (1) 0.2*M* HCOOH and 0.15*M* $HCOONH_4$, (2) 0.125*M* $HNO_3$ and 0.02*M* $(COONH_4)_2$, and (3) 1.0*M* $NH_4Cl$ and 0.01*M* $(COONH_4)_2$. Time periods of 10 to 60 min are required to deposit the films, which must then be removed from the cells before the electric circuit is interrupted to prevent their dissolution. Hydroxyl ions generated at cathode surfaces form metallic precipitates with current densities up to 300 $\mu$a/cm$^2$. A small concentration of uranium or magnesium assists film formation, which must be carried out in cells with a low ratio of electrolyte volume to cathode surface area such as 3 ml/cm$^2$. (W. H. Safranek)

## High-Energy-Rate Processes

Denver Research Institute[33] has explosively bonded lead to stainless steel despite their wide differences in sonic velocity. Bonding was obtained by using lead that had been prechilled with liquid nitrogen, whereas no bonding was obtained when the lead was at room temperature. Successful bonding was attributed to a 30% increase in the sonic velocity of the lead induced by chilling.

The feasibility of using explosive-welded bimetal inserts for joining large sections of steel to both titanium and aluminum was studied at the University of Missouri.[34] Sections of aluminum, titanium, and steel were welded to the explosively bonded inserts by either electron-beam or heliarc welding techniques and then evaluated with respect to the tensile strength of the explosive bond, accelerated-ambient-condition-corrosion resistance, and thermal-shock behavior. It was found that attaching segments to the insert by electron-beam welding caused very little degradation of the explosively produced bonds. For example, the bond in the aluminum and steel sample exhibited an ultimate tensile strength that was higher than the yield strength of the aluminum. However, the use of heliarc welding reduced the bond quality in both systems considerably.

The use of gaseous detonations as a high-energy forming technique has been studied at General American Transportation.[35] A sheet-metal blank and forming die were located at the end of an instrumented shock tube and then subjected to the impulse from a detonating methane/oxygen or propane/oxygen mixture. Materials formed during the test program include two high-strength steels and three titanium alloys. The results showed that this forming process has considerable potential, from both a technical and an economic point of view. (D. Laber)

## Welding and Brazing

### Electron-Beam Welding

Electron-beam welds between tubes of W–25 at.% Re–30 at.% Mo and T-111 (Ta–8 wt.% W–2 wt.% Hf)

**Table IV-1 Composition and Hardness of Refractory-Alloy Welds[28b]**

| Alloy composition, wt.% | Composition of weld,* at.% | Average hardness for 200-g load,† DPH |
|---|---|---|
| W–Re–Mo base alloy | 45 W, 25 Re, 30 Mo | 465 |
| T-111/Ta–8 W–2 Hf welded directly to W–Re–Mo alloy | 31.1 W, 5.6 Mo, 43.8 Ta, 18.5 Re | 840 |
| T-111 to W–Re–Mo with 0.018-in. transition of pure molybdenum | 17.6 W, 57.5 Mo, 15.4 Ta, 9.5 Re | 530 |
| T-111 to W–Re–Mo with 0.018-in. transition of Mo–50 Re | 19.0 W, 33.2 Mo, 23.3 Ta, 24.5 Re | 610 |

*At center of weld nugget and neglecting hafnium content.
†Average hardness across weld nugget.

are being investigated at Lawrence Radiation Laboratory.[28b] Both direct welding and 0.018 in.-thick transition members of molybdenum and a Mo–50 Re alloy have been used to join 0.5-in.-OD, 0.040-in.-wall tubes. All joints cracked on cooling because the alloys formed during fusion could not sustain shrinkage strains. Cracking was most severe in the direct weld and least severe in the pure-molybdenum transition weld. Electron fractography indicated that all joints failed by cleavage with no sign of ductile behavior. It was found that hardness varied directly with the amount of tantalum in the weld and that rhenium had little apparent influence on weld hardness, as shown in Table IV-1. It was believed that cracking might be prevented if a thicker molybdenum transition piece were used to dilute the tantalum or if welding conditions were developed to minimize alloying.

The quality of electron-beam-welded joints of Kovar and 321 stainless-steel tubes for an engine-cutoff sensor has been examined at Boeing.[36] The weld joint contained both a melt-through and a fillet weld. After visual and X-ray examination, hardness tests, and microscopic analysis, it was concluded that both welds were of excellent quality.

Westinghouse[37] has demonstrated the high joint efficiencies of electron-beam welds in 304 stainless steel. Welds were made on cold-rolled 304 stainless steel at 90, 60, 45, and 30° to the rolling direction, and their tensile and deformation properties were determined. Electron-beam welds of high depth-to-width ratios and reasonable scarf angles (45°) resulted in very high joint efficiencies, as shown in Table IV-2.

Experimental development of fuel-rod closure techniques using the plasma/electron-beam process has been conducted by The Babcock & Wilcox Co.[38] Welds have been made in both 304 stainless steel and Zircaloy-4. In the first of two approaches investigated, an end cap was welded to the fuel tube in an atmosphere of 300 ppm helium. A distortion-free joint was accomplished which eliminated additional machining to remove any upset or expelled material that would interfere with rod insertion or removal. In the second approach the end closure was formed from the tube itself.

**Table IV-2 Properties of Electron-Beam Welds in 304 Stainless Steel[37]**

| Type of specimen | Ultimate strength, 1000 psi | Uniform plastic elongation in the base metal, % | Nominal strain to fracture in 2-in. gauge length, % |
|---|---|---|---|
| Annealed and welded | 87.5 | 74 | 82.5 |
| Cold rolled and unwelded | 119.6 | 23 | 41.5 |
| Cold rolled and butt welded | 114 | 2.5 | 10.5 |
| Cold rolled and welded; scarf angle = 60° | 117.5 | 7 | 18.5 |
| Cold rolled and welded; scarf angle = 45° | 118.5 | 11.5 | 28.5 |
| Cold rolled and welded; scarf angle = 30° | 118.5 | 11.5 | 28.4 |

## Other Welding

A method for charging and sealing plutonium alloys into fuel elements while avoiding radioactive contamination of the container surface has been developed at Los Alamos.[39] GTA welding was used to seal the fuel elements in the special welding fixture shown in Fig. IV-2. This fixture permits welding in a high-quality inert atmosphere outside of the confines of a large glove box. The welding equipment used in this technique can accommodate a variety of container sizes and programmed welding currents from <10 amp to >200 amp. Typical welding parameters for containers in various materials and sizes are shown in Table IV-3.

The diffusion bonding of niobium and tantalum to themselves and to each other was investigated at RAI Research Corp.[40] The temperature at which diffusion-controlled bonding occurs with an intermediate bonding aid is substantially lower than the recrystallization

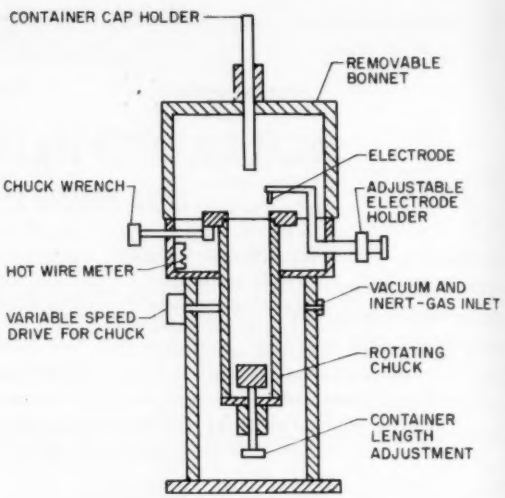
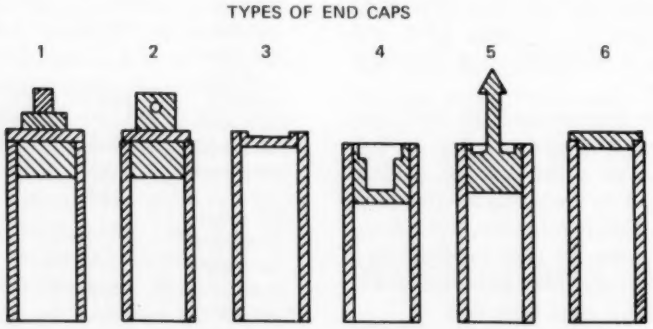



Fig. IV-2 Welding-fixture schematic.[39]

Table IV-3 Welding Parameters for Various Containers and End Caps[39]

| Container | | | | Welding time, sec | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| Material | Diameter, in. | Wall thickness, in. | Types of end caps | Up slope | Weld | Down slope | Container rotation sec/rev | Electrode diameter,* in. | Electrode gap, in. | Fixture position from vertical, deg | Current during welding, amp |
| Ta | 0.440 | 0.030 | 1 or 2 | 5 | 15 | 5 | 12 | 0.060 | 0.060 | 0 | 100 |
| Ta | 0.440 | 0.030 | 3, 4, or 5 | 5 | 13 | 5 | 10 | 0.060 | 0.050 | 0 | 40 |
| Stainless steel | 0.750 | 0.035 | 3, 4, or 5 | 5 | 20 | 5 | 16 | 0.020 | 0.050 | 0 | 15 |
| Stainless steel | 0.875 | 0.125 | 6 | 5 | 15 | 5 | 12 | 0.060 | 0.050 | 45 | 80 |
| Mild steel | 3.000 | 0.060 | 6 | 5 | 55 | 5 | 48 | 0.060 | 0.060 | 0 | 65 |
| Cu | 0.875 | 0.050 | 3 | 5 | 10 | 2 | 8 | 0.093 | 0.090 | 0 | 120 |
| Ni | 1.500 | 0.005 | 6 | 5 | 50 | 5 | 48 | 0.010 | 0.025 | 80 | 8 |
| Au | 0.750 | 0.030 | 3 or 4 | 5 | 15 | 5 | 12 | 0.040 | 0.020 | 0 | 36 |
| W | 0.750 | 0.060 | 3 | 5 | 23 | 5 | 18 | 0.125 | 0.125 | 0 | 165 |
| W† | 0.750 | 0.060 | 3 | 5 | 23 | 5 | 18 | 0.125 | 0.090 | 0 | 180 |




*Electrodes, 2% thoriated tungsten.
†Weld chamber at 6 in. abs. argon pressure.

temperature of the parent metals in the work-hardened condition: 419°C compared with 600°C for niobium and 800°C for tantalum. Using aluminum foils, good lap bonds were obtained in all three material combinations Nb–Nb, Ta–Ta, and Nb–Ta in 30 min at 2000 psi and 419°C. Under the same conditions but without the foil, no bonds were obtained in 2 hr. Butt joints made using the aluminum foil had tensile strengths of 12,000 psi for niobium and 19,850 psi for tantalum. The joint efficiency was poor because only a small fraction of available contact areas (from 10 to 50%) was bonded. Oxidation was believed to be the cause of this poor efficiency, and stricter atmosphere control and cleaning procedures were suggested as means of improvement.

A British patent[41] has been issued to cover the welding of a composite metal-oxide material such as SAP alloy to itself, a metal, an alloy, or another composite. One member is heated either to fusion or to a softening temperature, and the second member is gently immersed in the central area of the fused/softened zone for 5 to 6 min. The junction is then cooled in place and machined.

## Brazing

Brazing procedures for Inconel 718 have been developed for use with the Phoebus-2A reactor at Los Alamos.[42] In selecting a brazing alloy, the effects of both brazing temperature and alloy composition on base-metal strength were considered. Nickel-base brazing alloys were rejected because of the tendency of carbon, boron, and silicon to diffuse along grain boundaries, thereby reducing the ductile cross section of the assembly and possibly affecting both high-temperature and cryogenic strength. After preliminary investigation, an 82 Au–18 Ni alloy with a flow point of 1800°F (982°C) was chosen for all structural brazes, which were made in a single brazing step. For other joints, where structural strength was not a consideration, Au–8 Pd–22 Ni and Au–16.5 Cu–2 Ni were used. These alloys have flow points of 1920 and 1720°F (1049 and 938°C), respectively.

In the final procedure the surfaces were coated with 0.0005 in. of nickel to ensure good filler-metal flow during brazing in a cam-controlled, resistance-heated furnace containing high-purity argon (less than 1 ppm $H_2O$ and 2 ppm oxygen). Nearly 2000 assemblies have been brazed by this technique with less than 1% rejects. Tensile properties of assemblies using this and another brazing procedure are given in Table IV-4. Group I assemblies were brazed at 1920°F (1050°C) using Au–8 Pd–22 Ni alloy for structural brazes. Group II assemblies were brazed with Au–18 Ni alloy at 1830°F (1000°C). Both groups were heat-treated by holding at 1325°F (720°C) for 8 hr and then cooling at 20°F/hr (11°C/hr) to 1150°F (620°C). Elevated and cryogenic temperature properties for the Group II assemblies are shown in Table IV-5 and IV-6.

**Table IV-4 Average Room-Temperature Tensile Properties of Brazed and Heat-Treated Alloy 718 Assemblies[42]**

| Braze | Ultimate strength, 1000 psi | Proportional limit, 1000 psi | Yield strength (0.2% offset), 1000 psi | Elongation, % |
|---|---|---|---|---|
| | | Group I Specimen | | |
| Au–8 Pd–22 Ni | 185.9 | 96.7 | 151.5 | 10.1 |
| | | Group II Specimen | | |
| Au–18 Ni | 203.8 | 127.8 | 168.8 | 12.5 |

**Table IV-5 Average Elevated-Temperature Tensile Properties of Brazed and Heat-Treated Alloy 718 Assemblies[42]**

| Test temp., °F | Ultimate strength, 1000 psi | Yield strength (0.2% offset), 1000 psi | Initiation stress, 1000 psi |
|---|---|---|---|
| 70 | 194.3 | 172.1 | |
| 1000 ± 5 | 150.4 | 134.0 | 131.9 |
| 1325 ± 5 | 128.2 | 126.2 | |

**Table IV-6 Average Low-Temperature Tensile-Test Data on Brazed and Heat-Treated Assemblies[42]**

| Test temp., °K | Ultimate strength, 1000 psi | Yield strength (0.2% offset), 1000 psi | Elongation, % |
|---|---|---|---|
| | **Full-Length Brazed Assemblies** | | |
| 76 | 227.8 | 184.1 | 11.8* |
| | **Mockup Assemblies** | | |
| 300 | 199.4 | 163.7 | 15.2† |
| 20 | 268.6 | 199.2 | 14.9† |

*Elongation, full assembly.
†Elongation in 1-in. gauge length.

Joining procedures were developed at Garrett Corp.[43] for three nickel-base alloys in fabricating lightweight heat exchangers designed to withstand 100 hr of operation at 1540 to 2140°F (840 to 1170°C). For 0.003-in.-wall tubes of Hastelloy X, brazing with Nicrobraz 30 alloy (Ni–19 Cr–10 Si–1 Mo–4 Fe) at 2175°F (1190°C) in either a vacuum or dry-hydrogen atmosphere was found satisfactory. Tubes of L-605 alloy having wall thicknesses of 0.006 to 0.010 in. were brazed with J8102 alloy (Ni–15.2 Cr–8 Si) at 2200°F (1205°C). Again, both vacuum and dry-hydrogen atmospheres were satisfactory. Several welding processes also proved satisfactory with L-605, including inert gas–tungsten arc welding, spot welding, and laser welding. TD-nickel tubes with 0.006 to 0.008-in.-wall thicknesses were brazed in vacuum using TD-20 braze alloy (Ni–25 Mo–16 Cr–5 W–4 Si). However, excess quantities of the TD-20 alloy proved to be erosive to the TD nickel. During high-temperature exposure, oxidation of the TD nickel was accelerated at the base of the braze fillet, creating stress risers and limiting the service temperature of the uncoated structure to 1950°F (1065°C).

Unalloyed tantalum has been satisfactorily brazed to 316 stainless steel by NASA–Lewis.[44] Vacuum brazing was accomplished at 2150°F (1175°C) using J8400 brazing alloy (Co–21 Cr–21 Ni–8 Si–3.5 W–0.4 C–0.8 B). When flat sheet and tubular specimens were tested at 1350°F (730°C) in a vacuum chamber ($10^{-7}$ to $10^{-6}$ torr), all joints failed in the tantalum or stainless-steel parent metal. No unfavorable diffusion was observed between the braze alloy and the parent metals. It was also found that eliminating voids at the root of the tongue (tongue-and-groove joints) increased the ultimate strength of the joint because of increased effective cross-sectional area.

Solar[45] has developed a brazing process for attaching internal fins of Nb–1 Zr foil to Nb–1 Zr heat-receiver tubes. In brazing tests on T-joint and lap-joint specimens, 15 braze alloys (Cu, Au, Ti/Zr, and Zn bases) were evaluated. The three alloys that performed most satisfactorily in these tests together with the average tensile shear strengths of their respective brazed joints are:

| Alloy | Psi |
|---|---|
| Cu–2 Ni | 38,100 |
| Zr–25 V–16 Ti | 38,500 |
| Zr–25 V–16 Ti–0.1 Be | 37,600 |

Because of its braze fluidity and filleting characteristics, the Zr–25 V–16 Ti–0.1 Be alloy was used to braze full-scale heat-receiver tubes. Brazing was performed satisfactorily at 2130°F (1165°C) for 5 min in an induction furnace with a vacuum of $1 \times 10^{-5}$ torr. The specimens were enclosed in cylindrical tantalum susceptors to ensure uniform and rapid heating.

(J. E. Mortland and R. M. Evans)

# Nondestructive Testing

## Ultrasonic Techniques

Equipment is commercially available for measuring thicknesses down to 0.010 in. by ultrasonic means. Battelle–Northwest[46] applied critical-angle measurements using a dual-element probe to measure thicknesses ranging from 0.001 to 0.005 in. This method is believed applicable to measurement of coating thickness, if the velocity of a surface wave differs measurably between the coating and the substrate.

Battelle–Northwest has also adapted a conventional pulse-echo technique to test cylindrical isotope heat sources for weld penetration and cracks and other wall defects and to measure wall thickness.[47] It was initially designed for inspection of end-cap welds on the heat sources.

The nonlinear interaction between high- and low-frequency ultrasonic waves has been used by Lawrie[48] to enhance detection of imperfect bonds. The low-frequency wave perturbs the interface and produces modulation of the high-frequency transmitted wave.

It has been known for a long time that stress affects the velocity of sound in materials, but the

effect is so small that it is difficult to measure. Benson[49] has developed techniques by which relations between the ultrasonic velocity and stress have been established for a number of aluminum alloys. These techniques were applied to aluminum plates containing weldments. It was necessary to determine the orientation of the principal axes of stress and the effect of material properties such as grain orientation. The accuracy of measurements obtained ultrasonically compared favorably with those obtained by destructive tests. (D. Ensminger)

## NDT Methods Other Than Ultrasonics

A series of NASA classroom instruction manuals and tests on commonly used methods of nondestructive testing has been completed by General Dynamics and is available on microfiche. The titles and respective accession and report numbers are listed below.

| Title | Accession No. | NASA No. |
|---|---|---|
| Liquid Penetrant Testing | N68-28777 | CR-61205 |
| Magnetic Particle Testing | N68-28778 | CR-61206 |
| Eddy Current, Vol 1: Basic Principles | N68-28779 | CR-61207 |
| Eddy Current, Vol 2: Equipment, Methods, and Applications | N68-28780 | CR-61208 |
| Ultrasonics, Vol 1: Basic Principles | N68-28781 | CR-61209 |
| Ultrasonics, Vol 2: Equipment | N68-28782 | CR-61210 |
| Ultrasonics, Vol 3: Applications | N68-28783 | CR-61211 |
| Radiography, Vol 1: Origin and Nature of Radiation | N68-28784 | CR-61212 |
| Radiography, Vol 2: Radiation Safety | N68-28785 | CR-61213 |
| Radiography, Vol 3: Radiographic Equipment | N68-28786 | CR-61214 |
| Radiography, Vol 4: Making a Radiograph | N68-28787 | CR-61215 |
| Radiography, Vol 5: Film Handling and Processing | N68-28788 | CR-61216 |
| Magnetic Particle Testing: Classroom Training Manual | N68-28789 | CR-61227 |
| Liquid Penetrant Testing: Classroom Training Handbook | N68-28791 | CR-61229 |
| Eddy Current Testing: Classroom Training Handbook | N68-28792 | CR-61230 |
| Radiographic Testing: Classroom Training Handbook | N68-28793 | CR-61231 |

An eddy-current tubing tester using the multiple-parameter separation and suppression techniques previously developed at Hanford has been described by Battelle–Northwest investigators.[50] This two-channel, two-frequency instrument reduces the undesirable effect of test-probe wobble signals on both channels. A new analyzer circuit or signal transformation section is used for the successive elimination of parameters. The tester can be operated using either of its two test frequencies, 100 and 300 kc, singly or simultaneously. When the tester is operated in its single-frequency mode, two test parameters such as probe wobble and defects giving signals having components in quadrature with probe-wobble signals may be separated.

When the tester is operated in a two-frequency mode, the effect of one test parameter can be minimized, and the effects of two other test parameters may be determined. Results are given for the two-frequency mode of operation in which probe-wobble signals were minimized on both of the two output channels, while, at the same time, signals due to defects opening on the inner wall of the tubular test specimen appeared on one channel and signals due to defects opening on the outer wall of the specimen appeared on the other channel.

Acoustic emission has been studied at Battelle–Northwest[51] as an in situ nondestructive test for welds in stainless-steel plate. The method is aimed at detection of defects as they initially occur. A direct correlation was established between acoustic emission rate and radiographic analysis of single-pass machine welds in ⅛-in. 304L stainless-steel plate containing induced defects at specific locations. It was found that the onset of acoustic emission is delayed 20 to 45 sec as the defect region begins to cool and that during cooling the acoustic emission rate from induced defect regions increases to a peak at about 400°C. The acoustic emission rate from multipass welds in ½-in. 304L and 316 plates was greater than that from the single-pass welds by about an order of magnitude, and the same defect correlation between radiographic analysis and acoustic emission rate was observed.

The apparent propagation velocity of the acoustic pulses from the induced defect regions varied as much as a factor of 2, which suggests that the acoustic emission signals reach the receivers by indirect routes. The characteristic emission-pulse shape and spectral distribution vary with distance or direction from the acoustic emission source. Since pulse lengths are sufficient to set up complex reflection patterns in the plate, the received signal characteristics are determined by source location, receiver location, and plate geometry.

It was believed that this work established that it was possible to detect certain types of weld defects by acoustic emission monitoring. The primary advantage

noted for this technique is that defects can be detected during the welding process. Acoustic emission techniques appear to be sensitive to microfissures beyond the resolution limits of presently applied ultrasonic and radiographic methods. On that basis, this technique, used in conjunction with other weld-inspection methods, could reduce significantly the rejection rate in final inspection of welds. (A. F. Leatherman)

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